THE PREDICTION OF MULTICOMPONENT ION EXCHANGE EQUILIBRIA WITH PARTICULAR REFERENCE TO THE SYSTEM INVOLVED IN THE RECOVERY OF URANIUM

by

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PREFACE

I hereby declare that the material incorporated in this thesis is my own work and has not been submitted for a degree at any other university or institution.

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ABSTRACT

The problem of predicting the general ion exchange equilibria pertaining to systems of industrial significance is generated by the multicomponent nature of such systems and the nonidealities which may be present in both the solution and exchanger phases.

A general framework applicable to multicomponent systems incorporating nonideal effects in both phases is presented. For the solution phase a well established procedure for calculating activity coefficients is adopted. Deviations from ideal behaviour in the exchanger phase are modelled by the Wilson equation, which expresses the excess Gibbs free energy of mixing of the resinates as a function of composition. A significant advantage is afforded by this equation in that theoretically a multicomponent system may be predicted from the binary interaction coefficients of this equation which are determined experimentally, thereby reducing the otherwise extensive experimental program.

These ideas are applied to systems of increasing complexity from simple binary characterisation experiments to the prediction of a six component system related to that encountered in the recovery of uranium from sulphuric acid leach liquors.

Experimentation for the systems involving the ions SO_4^{2-}, Cl^- and NO_3^- and a strong base anion exchanger have provided a severe test for the procedure proposed. The agreement between the predicted and experimental resin phase composition data for this ternary system is within ± 5%.

The addition of complexing agents complicates the procedure in that it becomes physically impossible to decompose the system into the desirable

experimental binary systems. In this case higher order systems are characterised. Introducing a mineral acid to the ternary system discussed previously generates the HSO_4^- ion which necessitates the characterisation of other ternary systems before the quaternary system may be predicted. The agreement between the predicted and experimental resin phase composition for the quaternary system is shown to be within ± 10%.

The work is easily extended to include the more complex systems generated by the complexation of metal ions with the various ligands present. Provided the stoichiometry of the complex species in the exchanger phase is well defined the complexes present no difficulties in the characterisation procedures.

Experimental studies on the acidic uranyl sulphate quaternary system provide the desired ion exchange equilibrium constants and the interaction coefficients.

In order that the interaction coefficients for the ion pairs such as $UO_2(SO_4)_2^{2-}$, Cl^- and $UO_2(SO_4)_2^{2-}$, NO_3^- may be estimated it is necessary to characterise two quinary systems. Nevertheless the characteristics of lower order systems are employed to reduce the number of unknown parameters.

Finally it is possible to predict the resin phase composition of the six component system which results from chloride and nitrate species being included in the acidic uranyl sulphate system. The quantitative effects of all the components in the solution phase on the extent of uranium loading are predicted.

Although the ferric ion is an important component in the industrial

situation this ion has been excluded from this work because at this stage it is not possible to identify or measure the quantity of the various ferric complexes present in the resin phase for a particular solution condition.

NOMENCLATURE

Latin Symbols

a_j	ion size parameter in Debye-Huckel equation.
a'_j	activity of species j in solution mixture.
a_k	activity of species k in resin phase.
A	parameter in Debye-Huckel equation.
A_j	chemical species j in solution phase.
b_j	ion parameter in Debye-Huckel equation.
B	parameter in Debye-Huckel equation.
B_k	chemical species k in resin phase.
Capacity	equivalent capacity of resin.
C_j	molar concentration of species j in solution phase.
DVB	divinylbenzene.
f_i	fugacity of component i.
F	normalised sum of square errors function.
G	Gibbs free energy.
$\underline{G}$	specific Gibbs free energy.
$\overline{G}_i$	partial molar Gibbs free energy
ΔG^E	excess Gibbs free energy
I	ionic strength defined as $\frac{1}{2} \sum_i z_i^2 C'_i$
k	mole ratio of sulphate to bisulphate in the resin phase at equilibrium.
K_i	equilibrium constant of reaction i.
K	stability constant for complex formation.
M	number of species in resin phase.
n	total number of moles.

n'_j	number of moles of species j in solution.
n_k	number of moles of species k in resin.
N	solution normality.
N	number of independent reactions.
pH	$-\log a'_{H^+}$.
P	pressure.
Q	number of independent ion exchange reactions.
R	number of reactions.
R	gas constant.
RMS	root mean square error.
S	number of species in solution phase.
T	temperature.
V	volume.
x_i	mole fraction of species i in resin phase.
x'_i	mole fraction of species i in solution phase.
X_i	extent of reaction in moles.
y_i	equivalent fraction of species i in resin phase.
y'_i	equivalent fraction of species i in solution phase.
z_j	ionic charge of species j.

Greek Symbols

α_{ij}	stoichiometric coefficient of j th species in solution for i th competing reaction.
β_{ik}	stoichiometric coefficient of k th species in resin for i th competing reaction.
γ_k	activity coefficient of species k in resin phase.
γ'_j	activity coefficient of species j in solution phase.

λ_i	equilibrium quotient of i th reaction.
Λ_{ij}	Wilson interaction parameter.
ν	average ligand number in resin phase complex.
ξ_i	extent of reaction i in moles/l system.

Subscripts

exp	experimental value of variable.
fit	value of variable from curve-fitting procedures.
pred	predicted value of variable.

Superscripts

E	with operator Δ denotes the excess change in property upon mixing.
'	solution phase.
o	reference state or initial condition.
I	ideal case.
*	reference state or inferred value of variable.

Operators

Δ	finite change in state property.
Π	cumulative product operator.
Σ	cumulative summation operator.

CONTENTS

CHAPTER ONE

INTRODUCTION

Reactions at solid-liquid interfaces are used extensively in nature. In particular ion exchange reactions occur in soils and living organisms. Man has recognised this and has developed systems which exploit this phenomenon to his benefit.

Today ion exchange is an important unit operation in the process industries. Applications include the desalination and purification of water and the hydrometallurgical practices of recovery, purification and concentration of metals from aqueous media. Further, in the chemical, nuclear, food and pharmaceutical branches of industry and more recently in the treatment of effluents and trade wastes aspects of ion exchange technology have been applied.

The techniques and theory of ion exchange processes continue to advance. At present interest in continuous counter current ion exchange systems is increasing in some applications. HAINES *et al* (1973) has described a multistage continuous ion exchange system to treat acid pickle liquors and ROSS and GEORGE (1971) have applied this technique to the recovery of uranium from natural mine waters.

The mathematical representation of the ion exchange process has not been neglected. A general mathematical description of the isothermal ion exchange process has been formulated by SMIRNOV (1976). Included in the description are the important equations for thermodynamic equilibria and the kinetics of the process. This thesis is concerned solely with the thermodynamic equilibria of ion exchange systems.

The thermodynamic equilibrium aspects of ion exchange have been studied extensively both theoretically and experimentally as reviewed by

HELFFERICH (1962). More recently NOVOSAD (1973) studied the thermodynamics of ion exchange in the language of solution thermodynamics. Although a number of authors have investigated ternary systems (KLEIN *et al*, 1964, STREAT and BRIGNAL, 1970 and SOLDATOV and BYCHKOVA, 1971) the majority of published work is concerned with binary systems. This is surprising since ion exchange is predominant in the fields of hydrometallurgy and water treatment which generally comprise complex multicomponent systems.

KLEIN *et al* (1967) has presented a theoretical analysis of multicomponent ion exchange in fixed beds. The method is based on the assumption that the dimensionless selectivity coefficient is constant. Generally this is not true because nonidealities occur in both the solution and resin phase while the definition used for this coefficient makes no provision for including activity corrections. TONDEUR and KLEIN (1967) and HELFFERICH (1967) both presented generalised equilibrium theories for multicomponent ion exchange in fixed beds applied to systems with constant separation factors.

There is a need to develop a framework from which the general multicomponent ion exchange system, exhibiting non-ideal behaviour in both phases, may be predicted. An approach analogous to vapour-liquid equilibria, that a multicomponent system may be predicted from the combination of a number of non-ideal subsystems that are characterised experimentally, should be considered. This approach has the advantage of reducing the experimental program required to characterise a multicomponent system.

A second objective is to apply these ideas to the well known system encountered in the separation of uranium from sulphuric acid leach liquors. Absorption of uranium from sulphuric acid solution is the most

important ion exchange technique for uranium recovery.

It should be possible to quantify the effects, as reviewed by PREUSS and KUNIN (1958), of the solution characteristics of sulphuric acid leach liquors on uranium absorption by anion exchange resins. This could result in more efficient design procedures and operating conditions.

CHAPTER TWO

LITERATURE REVIEW

2.1 STUDIES OF NON-COMPLEXING SYSTEMS

An unnecessarily simplified approach to ion exchange equilibria is often adopted when the selectivity constant is defined in terms of concentrations of species in both phases. In general this results in the selectivity constant being a function of resin composition and total solution concentration as illustrated by BOARI *et al* (1974) in their studies of the simple SO_4^{2-} - Cl^- binary system.

The incentive to be able to predict multicomponent ion exchange from data of subsystems is great and has been attempted before. DRANOFF and LAPIDUS (1957) have investigated the ternary systems Dowex 50, Ag^+ - Na^+ - H^+ and Cu^{2+} - H^+ - Ag^+ at 0,1 N total concentration assuming unit activity coefficients of species in both phases. They report good agreement between ternary and binary data when presented as isotherms.

Similarly PIERONI and DRANOFF (1963) report that the system Dowex 50 - X8, H^+ - Na^+ - Cu^{2+} at 0,05 N and 0,1 N may be treated in terms of the binary systems. Effectively the third component is ignored in the graphical presentation when the ternary system is represented on a typical binary diagram by a single equilibrium line. However because of the assumption of unit activity coefficients in both phases it is not possible to calculate the equilibrium curve for a different total solution concentration.

Although DODDS and TONDEUR (1974) consider the ternary system Na^+ - Mg^{2+} - Ca^{2+} pertaining to the water softening process their procedure

effectively reduces the problem to a binary system.

Attempts have been made to remove the dependence of the binary equilibrium coefficient expressed in concentration units in both phases on the total solution concentration. This is achieved by introducing the activity coefficient of species in the solution phase. BARRER and KLINOWSKI (1974) have shown that for total solution concentrations of less than 2 N this is feasible. The resultant apparent equilibrium constant expressed in concentration of resin species and activity of solution species is then only a function of resin phase composition. However, NIKOLAYEV *et al* (1974) have shown for the system KU - 2 × 8, $CaCl_2$, HCl, H_2O at concentrations above 2 N that this condition does not hold and they suggest that the interactions of resin species are responsible. It is possible that this effect is due to the different water contents of the various ionic forms of the exchanger and/or the activity of water in the two pure electrolytes at finite concentrations is significantly different.

In the attempts to describe the functional relationship between resin phase composition and the variation of the selectivity coefficient corrected for solution phase non-idealities, statistical thermodynamic treatments have been proposed by BIRCH *et al* (1967) and extended in the temperature range 25° - 65°C by BIRCH *et al* (1969). Polynomial expressions are derived theoretically for the binary systems, chloride with each of the bivalent ions sulphate, oxalate, carbonate and borate. LEGENCHENKO (1971) has applied a statistical approach to describe the variation of the binary equilibrium constant, defined in terms of resin species concentrations and solution species activities, as a polynomial in the mole fraction of one resin species of degree not exceeding the coordination number. The equation provides opportunities for approximating to any dependence of the equilibrium constant on exchanger composition.

The statistical approaches reviewed have been restricted to binary systems.

SOLDATOV and BYCHKOVA (1970) have described the calculation of the ternary ion exchange system Dowex 50 - X10, K^+ - NH_4^+ - H^+ based on the concept that the activity coefficients in the binary mixture may be calculated from the experimental data and then used to find the corresponding quantities for the ternary mixture. For accurate results the treatment requires the main binary system be selected as that system closest to ideality.

A method has been proposed by DANES and DANES (1972) of calculating ion exchange equilibria of polyionic systems. The molar excess free mixing enthalpy of the resinates is expressed as a polynominal in the composition variables. In the case of a ternary system, for which the apparent equilibrium constants defined for solution activities and resin concentration of each of the binaries are not a linear function of composition, it is necessary to have ternary data as well.

BYCHKOVA and SOLDATOV (1973) successfully predicted the system KU - 2 × 25, NH_4^+ - Na^+ - H^+ from binary data with the use of two parametric lines of the Gibbs triangle related to the composition of the solution phase. It is required that one of these lines be rectilinear.

An approach which incorporates non-idealities in both phases of a multicomponent system without the limitations discussed will be more useful. KOKOTOV (1972) has discussed the methods for calculating the activity coefficients in the resin phase and the thermodynamic exchange constants. This system of equations includes non-idealities in both phases for multicomponent systems. This procedure is applied to the experimental data of multicomponent systems to obtain the activity

coefficients for each of the resinates.

The literature review so far describes methods of obtaining the thermodynamic equilibrium constants directly from ionic partition experiments. BOYD *et al* (1974) have developed a procedure to calculate the molal concentration product quotient K_m independently of direct measurements of the equilibrium and to predict the dependence of K_m on cross-linking and ionic composition.

2.2 STUDIES OF ION COMPLEXING SYSTEMS

Most aqueous phases exhibit some degree of complex formation between species. The studies reviewed in the previous section ignore this aspect or the authors indicate that complex formation is negligible.

TURNER (1968) has described a method to calculate the equilibrium diagram for systems involving weakly dissociated electrolytes. In this case a neutral complex is formed in the solution phase. The systems Zeo-Karb 225, acetic acid, sodium acetate and chloracetic acid, sodium chloroacetate were investigated, with cations H^+ and Na^+ being absorbed on the resin. The calculated and experimental results show good agreement.

A study has been made by GOLDEN *et al* (1974) to evaluate the behaviour of complexing systems in the solution phase for predicting the concentration history of the column effluent and composition profile in the column under local - equilibrium conditions. A ternary system with each cation forming a neutral complex with the single coion in the solution phase is discussed. In this treatment both separation factors and stability factors are presumed to be independent of mole fraction composition in the resin phase.

Complexation is not limited to the solution phase, both cationic and anionic complexes, particularly of metals may be present on ion exchangers. It is complexation in both phases which is responsible for the successful application of ion exchange in hydrometallurgy.

Ion pair formation or association in the resin phase is likely to occur if the fixed ionic groups are similar in structure to precipitating or complexing agents. Weakly basic and acidic resins are in this category. Reaction between carboxylic acid anions and H^+ is an example which has been studied by RUBINSHTEIN (1974). Essentially the interaction between counter ions and fixed ionic groups is separated from true ion exchange. In these studies the overall effect is characterised by the true exchange constants and the dissociation constants of the hydrogen or salt form of the ion exchange resin. The procedure allows for all interactions in the solution phase but only ion association in the resin phase, in other words the definition of the exchange constant includes activities of species in the solution phase and concentration units in the resin phase.

2.3 STUDIES INCLUDING URANYL SPECIES

The absorption of uranium from sulphuric acid solution is the most important ion exchange technique for uranium recovery.

In general the concentration of uranium, acid, sulphate, nitrate, chloride, ferric and other ions effects the equilibrium uranium loading. This has been concluded from reported operating plant experience and the numerous experiments conducted previously.

KORKISH (1970) has published a comprehensive review of the information available on the separation of uranium and thorium by means of ion exchange

resins. The review contains more than 800 references. Particular attention has been given to the anion exchange separation of uranium from sulphuric acid leach liquors.

At pH values below 2,5, ARDEN and WOOD (1956) and O'CONNOR (1954) conclude that uranium is absorbed from sulphate solutions by strong base anion exchange resins as the complex $UO_2(SO_4)_3^{4-}$.

ARDEN and WOOD (1956) ascribe the increased uranium loading at pH values in excess of 2,5 to the presence of $U_2O_5(SO_4)_3^{4-}$ on the resin. ARDEN and ROWLEY (1957) observed similar effects in work on systems with concentrated uranium solutions.

In the review KORKISH (1970) discusses the work of LING CHI 'IU *et al* (1965) in which it is shown that the species SO_4^{2-}, HSO_4^-, $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$ can exist in the resin phase depending on the experimental conditions. This has been confirmed by the investigation of MAJCHRZAK (1973) which also substantiates the observation of STEIN (1962) that the variation of the average number of sulphate ligands per uranium species is not significantly affected by the uranium concentration in the range 0,0005 to 0,005 M.

JURY and ADAMS (1959), DUNN (1959) and WATSON (1962) have also investigated this system.

YANO and KATAOKA (1960) in their extensive experimental program using Amberlite 400 and Duolite A101 exchangers suggest an optimum operational condition for the pure sulphuric acid leaching solution as: pH = 2,0 - 4,5, sulphate concentration expressed as SO_4^{2-}/UO_2^{2+} mole ratio, 1 - 15 and a UO_2SO_4 concentration of 2,0 - 4,0 g/l. The effect of temperature on the absorption isotherms was negligible in the range 10 - 45°C.

In most applications of this ion exchange process some recycling of the eluting solution occurs which results in nitrate and/or chloride being present. AYRES and WESTWOOD (1957) have quoted briefly work which shows that nitrate and chloride reduce the capacity of the resin for uranium with the nitrate ion having a greater effect than chloride ion.

KIKINDAI (1969) has investigated the system with nitrate ion included. The effects of the chloride and nitrate ion concentration on the uranium distribution coefficient has been reported by MAJCHRZAK (1973).

YANO *et al* (1960) studied the equilibria of this system with chloride - sulphate or nitrate - sulphate mixed forms of the strongly basic exchangers Amberlite 400 and Duolite A101. This work was extended by YANO and KATAOKA (1965), chloride or nitrate ions were introduced into the uranyl sulphate system. The experimental proportional constant or characteristic value of equilibrium was correlated separately for the chloride and nitrate form of the resin with pH, sulphate and uranyl ion concentrations of the solution phase. Unfortunately the data is presented graphically in the form of absorption isotherms for the uranium component alone.

Although a significant amount of work has been performed on the uranyl sulphate, sulphuric acid system including the addition of nitrate and chloride ions, no general quantitative method of predicting the composition of the resin phase at equilibrium with a known solution condition is available.

2.4 AIMS OF THE PRESENT INVESTIGATION

The aims of the present study are:

I. To extend the experimental data for the system related to that encountered in the recovery of uranium from leach liquors to include the five components uranium, acid, sulphate, chloride and nitrate ions.

II. To develop a means of quantitatively predicting the general ion exchange equilibrium based on a thermodynamic approach with expressions for the non-idealities evident in both phases.

III. To present the ion exchange characteristics such that they may be included in any future higher order system which has as components the species studied in this work.

CHAPTER THREE

THEORETICAL ASPECTS

3.1 THERMODYNAMIC SYSTEM

The ion exchange system consists of an aqueous phase containing a mixture of electrolytes in contact with a solid insoluble ion exchanger. The electrolytes in the aqueous phase may interact forming simple ions, complex ions or complex molecules.

There is a net transport of species between the resin and aqueous phases until equilibrium is established. At this stage the S species in the aqueous phase are identified as A_j while the M species bound to the fixed ionic groups R are identified as B_k. A schematic diagram Figure 3.1 illustrates the system.

SOLID RESIN PHASE	AQUEOUS LIQUID PHASE
$R\text{-}B_k$	A_j
n_k	n'_j
$k = 1,..,M$	$j = 1,..,S$

Figure 3.1 Thermodynamic system for ion exchange.

3.2 EQUILIBRIUM OF SIMULTANEOUS AND HETEROGENEOUS REACTIONS

If both the complex formation in solution and the ion exchange of species between phases are considered as chemical reactions then the general stoichiometric equation for several chemical reactions occurring simultaneously in either or both phases may be represented by

$$\sum_{j=1}^{S} \alpha_{ij} A_j + \sum_{k=1}^{M} \beta_{ik} B_k = 0 \qquad i = 1,..,R,..,N \tag{3.1}$$

where α_{ij}, β_{ik} are the stoichiometric coefficients of the species A_j in the aqueous phase and B_k in the resin phase respectively for the N reactions R of which are independent.

For a heterogeneous system , consisting of two phases, the Gibbs free energy can be written as

$$G = \sum_{j=1}^{S} n'_j \bar{G}'_j + \sum_{k=1}^{M} n_k \bar{G}_k \tag{3.2}$$

where the prime denotes the aqueous phase, n'_j is the number of moles of species A_j in the aqueous phase and n_k is the number of moles of species B_k in the resin phase. The partial molar free energy or chemcial potential is defined as

$$\bar{G}'_j = \left(\frac{\partial G}{\partial n'_j}\right)_{T,P,n'_{\ell\neq j},n} \quad , \quad \bar{G}_k = \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_{\ell\neq k},n'}.$$

Equilibrium of the system corresponds to the minimum in the Gibbs free energy of the system (BALZHISER *et al*, 1972). This condition is obtained by setting the derivative of G to zero so that

$$dG = 0 = \sum_{j=1}^{S} \bar{G}'_j \, dn'_j + \sum_{j=1}^{S} n'_j \, d\bar{G}'_j + \sum_{k=1}^{M} \bar{G}_k \, dn_k + \sum_{k=1}^{M} n_k \, d\bar{G}_k. \tag{3.3}$$

The Gibbs-Duhem equation reduces this to

$$\sum_{j=1}^{S} \bar{G}'_j \, dn'_j + \sum_{k=1}^{M} \bar{G}_k \, dn_k = 0. \tag{3.4}$$

If X_i is the extent of reaction i and n'^{o}_j, n^{o}_k are the initial number of moles of A_j and B_k respectively then

$$n'_j = n'^{o}_j + \sum_{i=1}^{R} \alpha_{ij} \, X_i \tag{3.5}$$

$$n_k = n^{o}_k + \sum_{i=1}^{R} \beta_{ik} \, X_i \tag{3.6}$$

Differentiating these expressions

$$dn'_j = \sum_{i=1}^{R} \alpha_{ij} \, dX_i \tag{3.7}$$

$$dn_k = \sum_{i=1}^{R} \beta_{ij} \, dX_i \tag{3.8}$$

Substituting Equation (3.7) and (3.8) in (3.4) yields

$$\sum_{j=1}^{S} \bar{G}'_j \sum_{i=1}^{R} \alpha_{ij} \, dX_i + \sum_{k=1}^{M} \bar{G}_k \sum_{i=1}^{R} \beta_{ik} \, dX_i = 0 \tag{3.9}$$

or

$$\sum_{i=1}^{R} \left(\sum_{j=1}^{S} \alpha_{ij} \, \bar{G}'_j + \sum_{k=1}^{M} \beta_{ik} \, \bar{G}_k \right) dX_i = 0 \tag{3.10}$$

Now, the R reactions are independent, so that this expression could not vanish through there being a set of dX_i such that $\left(\sum \alpha_{ij} + \sum \beta_{ik} \right) dX_i = 0$,

it can only vanish for arbitrary dX_i if (ARIS, 1965),

$$\sum_{j=1}^{S} \alpha_{ij} \overline{G}'_j + \sum_{k=1}^{M} \beta_{ik} \overline{G}_k = 0 \qquad i = 1,..,R \tag{3.11}$$

Expressions are required for the partial molar free energies which involve selection of the standard states.

3.3 EXPRESSION FOR THE PARTIAL MOLAR FREE ENERGY AND DEFINITION OF STANDARD STATES

For the perfect gas mixture DENBIGH (1966) gives,

$$\overline{G}_i = \underline{G}_i^{o} + RT \ln \overline{f}_i \,,$$

$$\overline{f}_i / p_i \to 1 \quad P \to 0 \tag{3.12}$$

where $\overline{f}_i$ is the fugacity of constituent i, p_i is the partial pressure and P is the total pressure. $\underline{G}_i^{o}$ is only a function of temperature.

An ideal solution is defined as one which obeys the LEWIS-RANDALL rule (BALZHISER *et al*, 1972).

$$\overline{f}_i = x_i f_i \tag{3.12a}$$

where f_i is the fugacity of the pure component in the same phase at the same temperature and pressure as the mixture, and x_i is the mole fraction of constituent i.

Then,

$$\overline{G}_i = \underline{G}_i^{*} + RT \ln x_i \tag{3.13}$$

$\underline{G}_i^*$ is a function of temperature and pressure since the relationship between mole fraction and fugacity is dependent on the total pressure of the system.

For non-ideal solutions Equation (3.13) is arbitrarily modified (GLASSTONE, 1942) by introducing the activity of constituent i

$$\overline{G}_i = \underline{G}_i^* + RT \ln a_i \tag{3.14}$$

or

$$\overline{G}_i = \underline{G}_i^* + RT \ln \gamma_i x_i \tag{3.15}$$

where a_i is the activity of constituent i and γ_i is the activity coefficient of constituent i such that

$$a_i = \gamma_i x_i \tag{3.16}$$

and $\underline{G}_i^*$ is only a function of temperature and pressure.

Thus the partial molar free energy is defined in such a way that the standard partial molar free energy is only a function of temperature and pressure and independent of composition. The magnitude of $\underline{G}_i^*$ and $RT \ln \gamma_i x_i$ are arbitrary in the sense that only their sum $\overline{G}_i$ is fixed.

For the standard state $a_i = 1$ and $\overline{G}_i = \underline{G}_i^*$

For the reference state $\gamma_i = 1$ and $a_i = x_i$ etc.

For the ionic species in the resin phase the pure component is selected as the standard state.

$$\overline{G}_k = G_k^* + RT \ln a_k \qquad (3.17)$$

$$= \underline{G}_k^* + RT \ln \gamma_k x_k \qquad (3.18)$$

with $\gamma_k \rightarrow 1$ as $x_k \rightarrow 1$.

For the ionic species and molecules in the aqueous phase the infinite dilution convention of DENBIGH (1966) is adopted

$$\overline{G}_j = \underline{G}_j^{\circ} + RT \ln a'_j \qquad (3.19)$$

$$= \underline{G}_j^{\circ} + RT \ln \gamma'_j C'_j \qquad (3.20)$$

with $\gamma'_j \rightarrow 1$ as $I \rightarrow 0$ where I is the ionic strength defined as

$$I = \frac{1}{2} \sum_j C'_j Z_j^2$$

The expressions for the partial molar free energies are substituted in Equation (3.11) to give

$$\prod_j a'^{\alpha_{ij}}_j \prod_k a_k^{\beta_{ik}} = K_i = \exp\left(- \frac{\sum_{j=1}^{S} \alpha_{ij} \underline{G}_j^{\circ} + \sum_{k=1}^{M} \beta_{ik} \underline{G}_k^*}{RT} \right) \qquad i = 1,..R \qquad (3.21)$$

where K_i is the thermodynamic equilibrium constant for the reaction i at temperature T and pressure P.

Expressed in terms of concentrations and activity coefficients Equation (3.21) is

$$K_i = \prod_j (\gamma'_j C'_j)^{\alpha_{ij}} \prod_k (\gamma_k x_k)^{\beta_{ik}} \qquad i = 1,..,R \qquad (3.22)$$

To obtain the equilibrium concentrations c'_j and x_k this set of R independent equations has to be solved.

3.4 SOLUTION OF THE SET OF SIMULTANEOUS REACTION EQUATIONS

That set of equilibrium concentrations which simultaneously satisfy the R equilibrium conditions is required.

The equilibrium constant is defined for each independent reaction of a set of simultaneous reactions in this two phase system.

$$K_i = \prod_j a'^{\alpha_{ij}}_j \prod_k a^{\beta_{ik}}_k \qquad i = 1,..,R \qquad (3.23)$$

or

$$K_i = \prod_j (\gamma'_j C'_j)^{\alpha_{ij}} \prod_k (\gamma_k x_k)^{\beta_{ik}} \qquad i = 1,..,R \qquad (3.24)$$

To solve these equations the equilibrium constant at temperature T and pressure P are required together with the relationships between c'_j and γ'_j and x_k and γ_k. The equations for the solution phase alone are well known. The experimental section of this work is concerned with obtaining the equilibrium constants for the combined resin and solution phase reactions and the relationship between γ_k and x_k.

With this information available it is possible to solve these reaction systems. A method or technique of solving these equations is required.

The calculation of complex chemical equilibrium has been reviewed by ZELEZNIK and GORDON (1968). More recently VAN ZEGGEREN and STOREY (1970) published a critical survey of the analytical techniques that have been developed for the computation of chemical equilibria.

ARIS (1965) describes the calculation of equilibrium compositions from simultaneous heterogeneous reactions using the concept of extent of reaction.

There are three situations considered in this work which require the solution of the simultaneous equations. The extents of reaction are defined differently in each case.

In the first case only the solution phase is considered. The extents of the P independent reactions are defined in concentration units, moles per litre of solution. From Equation (3.5)

$$n'_j = n'^{\circ}_j + \sum_{i=1}^{P} \alpha_{ij} X_i$$

dividing by the volume of the solution V

$$C'_j = C'^{\circ}_j + \sum_{i=1}^{P} \alpha_{ij} \xi_i \qquad (3.25)$$

where

$$\xi_i = X_i/V \qquad (3.26)$$

Equation (3.22) becomes

$$K_i = \prod_j \{\gamma'_j \, (C'^{\circ}_j + \sum_{i=1}^{P} \alpha_{ij} \xi_i)\}^{\alpha_{ij}} \qquad i = 1,..,P \qquad (3.27)$$

where

$$\gamma'_j = \gamma' \, (\underline{\xi})$$

At a given temperature and pressure there are P simultaneous non-linear equations to solve for the P equilibrium extents ξ_i. Included in the expression for the independent equilibrium reactions are the activity coefficients of the components in the solution phase which are functions of composition and hence extents. Thus the equations are implicit and numerical methods are required for solution. The methods used are reported in the Appendix I.

If at equilibrium the solution phase activities are known as is the case in column experiments then only the Q independent ion exchange reactions need be considered. Recalling Equation (3.6)

$$n_k = n_k^{\circ} + \sum_{i=1}^{Q} \beta_{ik} X_i$$

and since

$$x_k = \frac{n_k}{\sum_{k=1}^{M} n_k}$$

or

$$x_k = \frac{n_k^{\circ} + \sum_{i=1}^{Q} \beta_{ik} X_i}{\sum_{k=1}^{M} (n_k^{\circ} + \sum_{i=1}^{Q} \beta_{ik} X_i)} \tag{3.28}$$

then Equation (3.22) becomes

$$K_i = \prod_j a_j'^{\alpha_{ij}} \prod_k \left(\gamma_k \frac{n_k^{\circ} + \sum_{i=1}^{Q} \beta_{ik} X_i}{\sum_{k=1}^{M} (n_k^{\circ} + \sum_{i=1}^{Q} \beta_{ik} X_i)} \right)^{\beta_{ik}} \tag{3.29}$$

where

$$\gamma_k = \gamma(\underline{X})$$

At a given temperature T and pressure P there are Q simultaneous non-linear equations to solve for the Q equilibrium extents X_i. Included in the expression for the independent equilibrium reactions are the activity coefficients of the components in the resin phase which are functions of composition and hence extents. Thus the equations are implicit and numerical methods are required for solution.

For the situation where a specified amount of each phase of known composition is combined and equilibrium established extents are defined in moles.

Recalling Equation (3.5)

$$n'_j = n'^{o}_j + \sum_{i=1}^{R} \alpha_{ij} X_i$$

dividing by the volume of the solution phase, V

$$C'_j = C'^{o}_j + \frac{1}{V} \sum_{i=1}^{R} \alpha_{ij} X_i \qquad (3.30)$$

Equation (3.22) becomes

$$K_i = \prod_j \left(\gamma'_j \left(C'^{o}_j + \frac{1}{V} \sum_{i=1}^{R} \alpha_{ij} X_i \right) \right)^{\alpha_{ij}} \prod_k \left(\gamma_k \frac{n_k^{o} + \sum_{i=1}^{R} \beta_{ik} X_i}{\sum_{k=1}^{M} \left(n_k^{o} + \sum_{i=1}^{R} \beta_{ik} X_i \right)} \right)^{\beta_{ik}}$$

$$i = 1,..,R \qquad (3.31)$$

where

$$\gamma'_j = \gamma'(\underline{X}) \text{ and } \gamma_k = \gamma(\underline{X})$$

At a specified temperature and pressure there are R simultaneous non-linear equations to solve for the R equilibrium extents X_i.

Activity coefficients in both phases are functions of the extents X_i. Implicit numerical methods are required to obtain a solution.

In finding the independent reactions and using their extents as variables the number of reactions is minimized and the calculations simplified.

The successful application of this general framework depends on the availability of models to calculate the activity coefficients in both phases for multicomponent systems. In the following sections consideration will be given to these aspects.

3.5 ACTIVITY COEFFICIENTS IN THE SOLUTION PHASE

In the multicomponent solutions of industrial interest electrolyte concentrations are relatively high making the activity coefficients difficult to obtain either theoretically or from experimental data.

BROMLEY (1972) has estimated approximate individual ion values of β or B used in the extended Debye-Huckel theory for univalent aqueous solutions.

MEISSNER and KUSIK (1972) relate the mean activity coefficient of strong electrolytes to the reduced activity coefficient. The reduced coefficient of an electrolyte in a mixed solution is then estimated from the ion fractions in ionic strength units and the reduced coefficient of the electrolyte in a pure solution at the same ionic strength and temperature. Reasonable success is reported even at high electrolyte concentrations.

A generalised correlation for activity coefficient is presented by BROMLEY (1973) for single and multicomponent systems. Correlations with one parameter are possible up to ionic strength of six. However for bivalent metal sulphate and sulphuric acid the results are not satisfactory.

Equations for the accurate estimation of the activity coefficient ratios in ion exchange problems have been reported by PAL *et al* (1974).

KUSIK and MEISSNER (1975) have reviewed the calculation of activity coefficients in hydrometallurgy. Examples of some multicomponent systems have given estimates of the activity coefficients with errors within 20% of the measured quantities.

Recently SENGUPTA *et al* (1975) have applied the concept of ionic interaction coefficients to activity calculations in mixed electrolyte solutions of ion exchange systems.

A somewhat simplified approach applicable to multicomponent systems has been applied by TRUESDALL and JONES (1973) in the development of a computer program to calculate the chemical equilibria of natural waters.

The availability of the parameters required in this treatment when applied to the system under consideration in this work and the relatively small effect of the activity ratio on the equilibrium quotient for ion exchange reactions as shown by BARRER and KLINOWSKI (1974) has resulted in the use of this slightly less accurate method.

An expression for the single ion activity coefficient is obtained from the Debye and Huckel theory. The extended equation with two parameters per ionic component is (ROBINSON and STOKES, 1959)

$$\ln \gamma_j' = \frac{- A z_j^2 \sqrt{I}}{1 + Ba_j\sqrt{I}} + b_j I \qquad (3.32)$$

where I is the ionic strength of the solution

z_j is the ionic charge of the species j

A and B are temperature dependent parameters

a_j and b_j are the ion parameters.

TRUESDALL and JONES have calculated the parameters a_j and b_j from experimental mean salt activity coefficients. These parameters are quoted in Appendix A.2.

Thus with the two parameters per ionic species and the ionic strength of the solution it is possible to estimate the activity coefficient and hence the activity of each species in a multicomponent system. The calculation is iterative, the ionic strength being recalculated at each step until convergence is achieved.

3.6 ACTIVITY COEFFICIENTS IN THE RESIN PHASE

DAVIDSON and ARGENSINGER (1953), HOGFELDT (1953) and GAINES and THOMAS (1953) have in principle solved the problem of calculating the equilibrium constant and activity coefficients of the resin phase components from experimental ion exchange data. For a binary system the Gibbs-Duhem equation and the equation for the thermodynamic ion exchange equilibrium constant are solved. More recently SOLDATOV and BYCHKOVA (1971) have extended the method to multicomponent systems. The method is used to calculate the activity coefficients from multicomponent

data.

SOLDATOV (1972) has stated that despite the validity of the method adopted by the previous authors, the final results are incorrect or approximate since assumptions have been made without proof.

FREEMAN (1961) has derived expressions for the dependence of the logarithms of the activity coefficients of a binary system upon the equivalent fraction of the counter-ion in the exchanger. These expressions are based on the excess free energy of the resinates, expressed as a polynomial. The coefficients are derived from experimental measurements of the solution species activities at different exchanger compositions.

The basis of this method has been extended to multicomponent systems incorporating a model for the excess free energy which is applicable to multicomponent systems.

The excess mixture properties are useful in describing non-idealities of solid phases. The activity coefficients are generated from the functional relationship between the excess property and composition.

An excess property is the difference between the actual change of an extensive property upon mixing and the change that would occur if the solution were ideal at the same temperature and pressure.

The excess Gibbs free energy is given by

$$\Delta G^{E} = (\Delta G)^{\text{real}}_{\text{mixing}} - (\Delta G)^{\text{ideal}}_{\text{mixing}} \qquad (3.33)$$

For the resin phase excluding the solvent, water in this case, we have

$$G_{Mixture} = \sum_{i=1}^{M} n_i \bar{G}_i \tag{3.34}$$

$$G_{Components} = \sum_{i=1}^{M} n_i \underline{G}_i \tag{3.35}$$

The change in the Gibbs free energy for the ideal case is

$$\Delta G^I = \sum_{i=1}^{M} n_i \left(\bar{G}_i - \underline{G}_i\right)^I \tag{3.36}$$

For the ideal case $\bar{G}_i - \underline{G}_i = RT \ln x_i$

$$\Delta G^I = \sum_{i=1}^{M} n_i \left(RT \ln x_i\right) \tag{3.37}$$

The excess Gibbs free energy of the mixture is

$$\Delta G^E = \Delta G - \Delta G^I$$

$$= \sum_{i=1}^{M} n_i \left(\bar{G}_i - \underline{G}_i - RT \ln x_i\right) \tag{3.38}$$

Introducing the activity coefficient γ_i

$$\bar{G}_i - \underline{G}_i = RT \ln \gamma_i x_i \tag{3.39}$$

we obtain

$$\Delta G^E = \sum_{i=1}^{M} n_i RT \ln \gamma_i$$

or

$$\Delta \underline{G}^E = \sum_{i=1}^{M} x_i RT \ln \gamma_i \tag{3.40}$$

The partial excess Gibbs free energy is

$$\overline{\Delta G}_j^E = \left(\frac{\partial\, \Delta G^E}{\partial\, n_j}\right)_{P,T,n_k}$$

$$= \sum_{i=1}^{M} RT\ \ell n\ \gamma_i \left(\frac{\partial n_i}{\partial n_j}\right)_{P,T,n_k} + \sum_{i=1}^{M} n_i\ RT \left(\frac{\partial\ \ell n\ \gamma_i}{\partial\, n_j}\right)_{P,T,n_k} \tag{3.41}$$

Now $$\left(\frac{\partial\, n_i}{\partial\, n_j}\right)_{P,T,n_k} = 0 \qquad \text{unless} \quad i = j \tag{3.42}$$

Also $$\sum_{i=1}^{M} n_i\ RT \left(\frac{\partial\ \ell n\ \gamma_i}{\partial\, n_j}\right)_{P,T,n_k} = RT\ n \sum_{i=1}^{M} x_i \left(\frac{\partial\ \ell n\ \gamma_i}{\partial\, n_j}\right)_{P,T,n_k} = 0 \tag{3.43}$$

since the Gibbs-Duhem equation gives

$$\sum_{i=1}^{M} x_i \left(\frac{\partial\ \ell n\ \gamma_i}{\partial\, n_j}\right)_{P,T,n_k} = 0 \tag{3.44}$$

Thus

$$\overline{\Delta G}_j^E = \left(\frac{\partial\, \Delta G^E}{\partial\, n_j}\right)_{P,T,n_k} = RT\ \ell n\ \gamma_i \tag{3.45}$$

This result implies that we require the excess Gibbs free energy of a mixture as a function of composition to determine the activity coefficients of each of its components.

The functional relationship between the Gibbs free energy and composition must satisfy the following conditions.

If the pure-component standard state at the temperature and pressure of the system is used then $\gamma_i \to 1$ as $x_i \to 1$. As $x_i \to 1$ all other

compositions approach zero therefore $\Delta\underline{G}^E = 0$ for pure components.

In general

$$\frac{\Delta\underline{G}^E}{RT} = \phi\,(x_1,..,x_M) \tag{3.46}$$

where

$$\frac{\Delta\underline{G}^E}{RT} = 0 \text{ for any } x_i = 1$$

The WILSON (1964) model has been selected to correlate the excess Gibbs free energy. This equation is a semi-empirical generalization of the FLORY (1941, 1942) and HUGGINS (1941) equations and has been successfully applied to vapour-liquid equilibria (PRAUSNITZ *et al*, 1967).

The Wilson equation with two adjustable parameters per binary is

$$\frac{\Delta\underline{G}^E}{RT} = -\sum_{i=1}^{M} x_i \ln\left(\sum_{j=1}^{M} \Lambda_{ij}\, x_j\right) \tag{3.47}$$

Differentiating this expression gives

$$\ln \gamma_i = 1 - \ln\left(\sum_{j=1}^{M} x_j\, \Lambda_{ij}\right) - \sum_{k=1}^{M}\left(\frac{x_k\, \Lambda_{ki}}{\sum_{j=1}^{M} x_j\, \Lambda_{kj}}\right) \tag{3.48}$$

Only binary interaction parameters Λ_{kj} and Λ_{ki} appear, the parameters Λ_{ii}, Λ_{jj}, Λ_{kk} etc. are equal to unity.

The Wilson model for a multicomponent system requires only parameters which can be obtained from binary mixture data. This feature significantly reduces the experimental program required to characterise a multicomponent system.

The model has its theoretical origin as an athermal solution theory. This makes it particularly applicable to ion exchanger systems since generally heats of mixing are small (HELFFERICH, 1962).

The relationships between activity coefficients and composition have been described for both phases.

Equilibrium constants for the solution phase reactions are well tabulated, refer to Appendix A.1. The activity coefficients in the solution phase may be estimated from a well-known model and published parameters, refer to Appendix A.2. However the ion exchange reaction equilibrium constants are generally not available. For the activity coefficients in the resin phase a model has been proposed which requires ionic interaction parameters, these are also unavailable.

The following section outlines an approach adopted to obtain these parameters from experimental data.

3.7 PARAMETER ESTIMATION

The expression for the thermodynamic equilibrium constant Equation (3.22) is rearranged in terms of the experimentally accessible equilibrium quotient λ_i.

From equation (3.22)

$$K_i = \prod_j a'^{\alpha_{ij}}_j \prod_k x_k^{\beta_{ik}} \prod_k \gamma_k^{\beta_{ik}} \qquad i = 1,..,R \qquad (3.49)$$

introducing the equilibrium quotient λ_i

$$K_i = \lambda_i \prod_k \gamma^{\beta_{ik}} \qquad i = 1,..,R \qquad (3.50)$$

$$\lambda_i = \prod_j a'^{\alpha_{ij}}_j \prod_k x_k^{\beta_{ik}} \qquad i = 1,..,R \qquad (3.51)$$

and

$$\lambda_i = K_i \prod_k \gamma_k^{-\beta_{ik}} \qquad i = 1,..,R \qquad (3.52)$$

Provided the activity coefficient in the solution phase can be calculated λ_i may be determined from the ion exchange experiments. For a specified temperature and pressure the equilibrium quotient is related to the equilibrium constant and the activity coefficient in the resin phase.

Substituting Equation (3.48) into (3.52) yields

$$\ell n\ \lambda_i = \ell n\ K_i - \sum_{k=1}^{M} \beta_{ik} \left(1 - \ell n \left(\sum_{\ell=1}^{M} x_\ell\ \Lambda_{k\ell} \right) - \sum_{n=1}^{M} \left(\frac{x_n\ \Lambda_{nk}}{\sum_{\ell=1}^{M} x_\ell\ \Lambda_{n\ell}} \right) \right)$$

$$i = 1,..R \qquad (3.53)$$

Now since λ_i and x_k are experimental values, β_{ik} are known stoichometric coefficients, the parameters to be estimated are K_i and the binary interaction coefficients Λ_{kj}.

The same numerical methods applied to the solution of the simultaneous equations are used to estimate the parameters. In this case the objective function F is the square of the normalised error of the calculated and experimental equilibrium quotients.

$$F = \sum_{i=1}^{R} \left(\frac{\lambda_i^{exp} - \lambda_i^{calc}}{\lambda_i^{exp}} \right)^2 \qquad (3.54)$$

The calculated equilibrium quotients are given by Equation (3.53) A search is made for the K_i and set of interaction parameters λ_{kj} which minimise the function F.

For the case where K_i is specified the λ_{kj} are the only parameters to be estimated.

Data processing has two aspects therefore,

(a) Selection of the best set of parameters. Values determined from these parameters for resin composition are referred to in the experimental section as fitted values which when compared to the experimental values from which they were derived provides a basis for estimating the effectiveness of the regression procedures.

(b) It is possible by using lower order systems to infer all the interaction parameters required to specify a higher order system. The values predicted in this way are referred to as predicted values which when compared with experimental values obtained for the higher order system provide a severe test of the linearized procedure employed.

An extensive experimental program designed to substantiate the ideas expressed in this chapter is discussed in the following chapters.

CHAPTER FOUR

INVESTIGATION OF BINARY AND TERNARY SYSTEMS

The objective of the following experimental program is to determine whether the Wilson model satisfactorily characterises binary ion exchange systems. Thereafter a comparison is made between predictions of the ternary system based on the binary characteristics, and experimental data.

Binary systems involving SO_4^{2-}, NO_3^- and Cl^- ions have been selected because these three simple ions are present in typical uranium leach liquors and as such represent the smallest sub-systems of this multiionic system.

4.1 CHARACTERISATION EXPERIMENTS

4.1.1 Characterisation of the binary system SO_4^{2-} - NO_3^-

Ion exchange equilibria are determined for the system Amberlite 400, 0,2, 0,4, 0,6 N mixtures of Na_2SO_4 and $NaNO_3$ at 298^oK. The equilibrium reaction for this system is represented by

$$R_2SO_4 + 2NO_3^- \rightleftarrows 2RNO_3 + SO_4^{2-} \qquad (4.1)$$

where R is the fixed ionic group of the exchanger.

The thermodynamic equilibrium constant for this reaction is

obtained from the general expression, Equation (3.21)

$$K^{NO_3}_{SO_4} = \frac{a^2_{NO_3}\ a'_{SO_4}}{a_{SO_4}\ a'^{2}_{NO_3}} \qquad (4.2)$$

and the equilibrium quotient is obtained from the general expression Equation (3.51)

$$\lambda^{NO_3}_{SO_4} = \frac{x^2_{NO_3}\ a'_{SO_4}}{x_{SO_4}\ a'^{2}_{NO_3}} \qquad (4.3)$$

The charge balance equation of the species bound to the fixed ionic group R at equilibrium is

$$2c_{SO_4} + c_{NO_3} = \text{capacity} \qquad (4.4)$$

where c_i is the concentration of species i in the echanger phase expressed as mole i/l resin. One complex reaction occurs in the solution phase

$$Na^+ + SO_4^{2-} \rightleftarrows Na\ SO_4^- \qquad (4.5)$$

the stability constant for this reaction is tabulated in Appendix A.1. It is assumed that this relatively weak anionic complex is not absorbed by the exchanger.

Ions present in the solution phase are SO_4^{2-}, NO_3^-, Na^+ and $NaSO_4^-$, the parameters required for the Debye-Huckel equation for these ions are tabulated in Appendix A.2.

A. EXPERIMENTAL

The relationship between the resin and solution phase compositions at equilibrium may be determined in a number of ways. The batch method has been investigated by GARNETSKI (1974). A given quantity of exchanger of known composition is added to a specified solution of known composition and agitated. Once equilibrium is achieved the composition of the solution and exchanger are determined.

For the systems KU - 2, K^+ - Rb^+ and Na^+ - Rb^+ it has been experimentally confirmed that the relative error in determining the equilibrium constants by this method depends on the value of the parameter h defined as the ratio of initial total moles in solution to the initial total moles in the resin. Satisfactory precision may be obtained when h is very much less than 1,0. A disadvantage of the method is that the composition of the solution once equilibrium is achieved may not be predicted beforehand.

KLAMER *et al* (1958) discuss an elegant method which generates the desired relationship from a continuous elution curve. The limited application of the method is a disadvantage.

A more widely used technique is the column method described by KLAMER *et al* (1958). A solution having a known composition is passed through a column of ion exchanger until the composition of the effluent becomes equal to that of the feed. The major advantage of the method is that the solution composition at equilibrium may be specified beforehand.

The column technique is used to determine the ion exchange equilibria of the systems discussed in this work.

A description of the apparatus used to obtain the ion exchange data is given in Appendix B. The apparatus is designed to allow up to six tests to be performed concurrently. A description of the chemicals used is given in Appendix D. A detailed description of the procedure is presented in Appendix C. Capacity determinations are usually performed before the equilibriations as described in Appendix C.8. Equilibrium period is fixed at 48 hours as discussed in Appendix C.4. The elution solution for this system is 1M NaCl. The sulphate concentration on the resin is obtained from the sulphate analysis of the eluate according to the method outlined in Appendix E.2. The nitrate concentration in the resin is obtained by difference from the charge balance Equation (4.4)

$$c_{NO_3} = \text{Capacity} - 2\, c_{SO_4}$$

The column technique allows the calculation of activities in the solution phase independently of the results of the equilibrium tests. For this single complex, four component solution phase, the activities have been calculated according to the method described in Section 3.4.

It is not feasible to tabulate all the solution phase activity data. A specimen calculation for this system is presented in Appendix J.2.1.A. for the first experimental condition in Table 4.1.

4.1.2 Characterisation of the binary system SO_4^{2-} - Cl^-

Ion exchange equilibria are determined for the system Amberlite 400, 0,2 and 0,4 N mixtures of Na_2SO_4 and NaCl at 298°K. The equilibrium reaction for this system is represented by

$$R_2SO_4 + 2Cl^- \rightleftarrows 2RCl + SO_4^{2-} \tag{4.6}$$

The thermodynamic equilibrium constant for this reaction is obtained from the general expression Equation (3.21)

$$K_{SO_4}^{Cl} = \frac{a_{Cl}^2 \; a'_{SO_4}}{a_{SO_4} \; a'^2_{Cl}} \tag{4.7}$$

and the equilibrium quotient is obtained from the general expression Equation (3.51)

$$\lambda_{SO_4}^{Cl} = \frac{x_{Cl}^2 \; a'_{SO_4}}{x_{SO_4} \; a'^2_{Cl}} \tag{4.8}$$

The charge balance equation of the species bound to the fixed ionic group R at equilibrium is

$$2c_{SO_4} + c_{Cl} = \text{Capacity} \tag{4.9}$$

A single complex reaction occurs in solution as in the previous system according to Equation (4.5).

A. EXPERIMENTAL

The elution solution for this system is 1N $NaNO_3$. The chloride concentration in the eluate is obtained according to the method described in Appendix E.3. The sulphate concentration of resin is inferred from the charge balance equation (4.9)

$$c_{SO_4} = \frac{\text{Capacity} - c_{Cl}}{2.0}$$

4.1.3 Characterisation of the binary system NO_3^- - Cl^-

Ion exchange equilibria are determined for the system Amberlite 400, 0,2 and 0,4 N mixture of $NaNO_3$ and NaCl at 298°K.

The equilibrium reaction for this system is represented by

$$RCl + NO_3^- \rightleftarrows RNO_3 + Cl^- \qquad (4.10)$$

The thermodynamic equilibrium constant for this reaction is obtained from the general expression Equation (3.21)

$$K_{Cl}^{NO_3} = \frac{a_{NO_3}\ a'_{Cl}}{a_{Cl}\ a'_{NO_3}} \qquad (4.11)$$

and the equilibrium quotient is obtained from the general expression, Equation (3.51)

$$\lambda_{Cl}^{NO_3} = \frac{x_{NO_3}\ a'_{Cl}}{x_{Cl}\ a'_{NO_3}} \qquad (4.12)$$

The charge balance equation of the species bound to the fixed ionic group R at equilibrium is

$$c_{NO_3} + c_{Cl} = \text{Capacity} \qquad (4.13)$$

For this system no complexes are formed in the aqueous phase. The activities of the nitrate and chloride ion are easily calculated explicitly from the ionic strength, as shown in Appendix J.3.

A. EXPERIMENTAL

The elution solution for this system is 1 N $NaNO_3$. The chloride concentration of the known volume of eluate is analysed according to the method described in Appendix E.2.

The nitrate concentration of the resin phase is inferred from the equivalent balance Equation (4.13)

$$c_{NO_3} = \text{Capacity} - c_{Cl}$$

The results obtained for the three binary systems are reported and discussed together.

4.1.4 Results and discussion

Before the results are presented and discussed, it is essential to clarify the nature of the data presented. The data is reported in three categories, experimental fitted and predicted.

The following notation has been adopted throughout this thesis.

Experimental data is that obtained from measurements. If the particular variable is directly measurable the data is not qualified. If the value of the variable has been inferred from measured data then the data is qualified with an asterisk as superscript. For example, C_{HSO_4} is the directly measured concentration of the bisulphate ion on the resin while $C^*_{SO_4}$ refers to the concentration of sulphate ion on the resin determined from say an equivalent balance equation.

In the case where an experimental variable contains both types, then the data is qualified with 'exp' as subscript.

Fitted data is that obtained when the parameters estimated by curve-fitting procedures are substituted back into the expressions used in the curve-fitting. This data is qualified with 'fit' as a subscript.

Predicted data is that which is generated for multicomponent systems from the combination of parameters which are estimated from experimental data of systems of lower order. The data is qualified with 'pred' as a subscript.

The definition of the equilibrium quotient includes the experimental resin phase data expressed in mole fractions. In some instances the mole fraction of a species is inferred from an equivalent balance. An error introduced here or in the direct measurement will be compounded when inserted in the expression for the equilibrium quotient by the algebraic operations of division and exponentiation, particularly for multivalent exchange systems.

Thus the experimental data expressed as equilibrium quotients

is very sensitive to the resin phase composition variables and scatter in the experimental results is inevitable as illustrated by PAL *et al* (1974) and FREEMAN (1961). Notwithstanding this the data is used in this form in the least-squares estimation of the parameters. A comparison is made of the fitted and experimental equilibrium quotients and of the fitted and experimental resin phase compositions.

The experimental equilibrium composition of the resin and solution phases at the solution normalities specified are summarised in Table 4.1 for the three binary systems SO_4^{2-} - NO_3^-, SO_4^{2-} - Cl^- and Cl^- - NO_3^-.

From the basic equilibrium data the equilibrium quotients are determined for each equilibrium condition. A specimen calculation of the equilibrium quotient for the first experimental condition of the SO_4 - NO_3 system in Table 4.1 is given in the Appendix J.4.

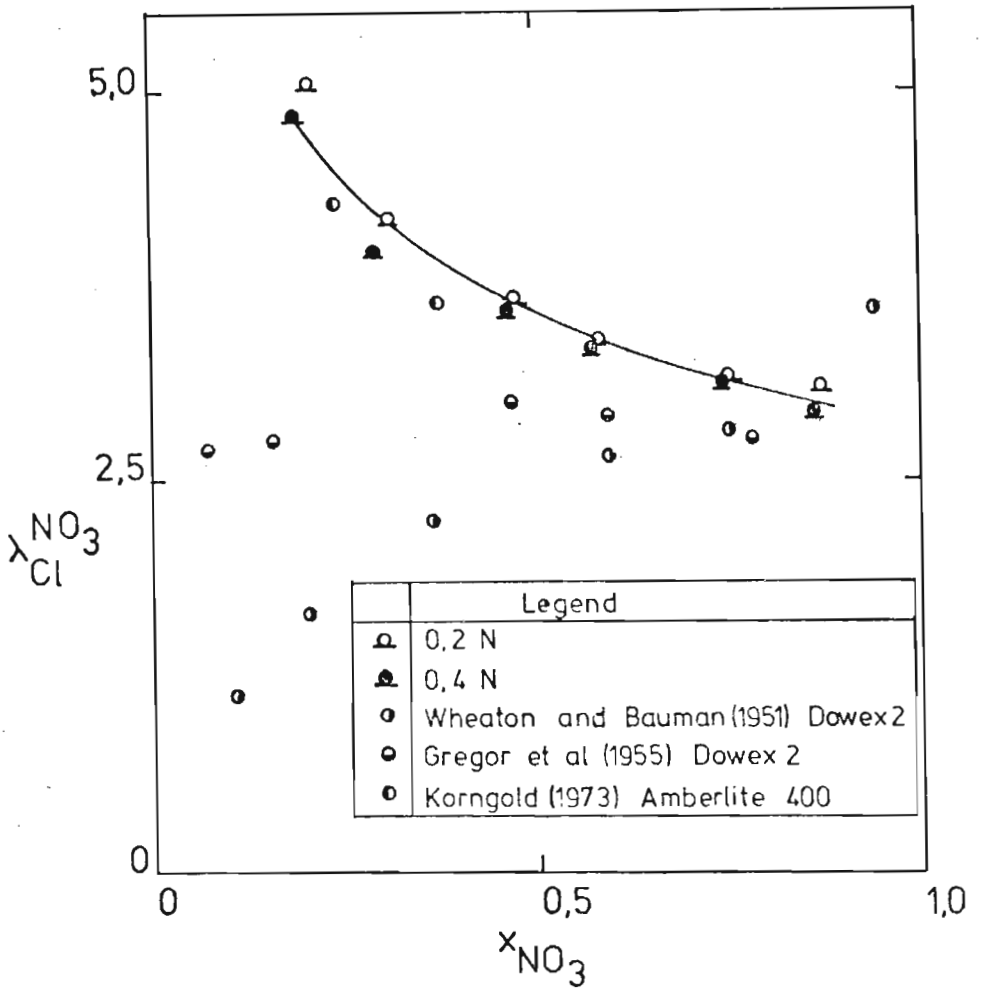
The variation of the experimental equilibrium quotients with composition in the resin phase for the binary systems is illustrated in Figures 4.1, 4.2 and 4.3. It can be seen that the data for the SO_4^{2-} - Cl^- system falls within the range of the published data of WHEATON and BAUMAN (1951) and O'CONNOR (1954). The data of O'CONNOR (1954), for the SO_4^{2-} - Cl^- system and KORNGOLD (1973), for the system NO_3^- - Cl^- is reported for samples of Amberlite 400 with 8% DVB. It can be seen that in both cases the experimental data reported for this work, which employs the same resin, is consistent with that of these two workers.

The deviation of this work from that of WHEATON and BAUMAN (1951) and GREGOR *et al* (1955) is acceptable since although also a polystyrene

Solution Normality N	SO_4^{2-} - NO_3^-				SO_4^{2-} - Cl^-				Cl^- - NO_3^-			
	Solution Equivalent Fraction		Resin Mole Fraction		Solution Equivalent Fraction		Resin Mole Fraction		Solution Equivalent Fraction		Resin Mole Fraction	
	ΣSO_4	NO_3	SO_4	NO_3^*	ΣSO_4	Cl	SO_4^*	Cl	Cl	NO_3	Cl	NO_3^*
0,2	0,90	0,10	0,401	0,599	0,90	0,10	0,721	0,279	0,95	0,05	0,794	0,206
	0,80	0,20	0,259	0,741	0,80	0,20	0,553	0,447	0,90	0,10	0,689	0,311
	0,60	0,40	0,119	0,881	0,60	0,40	0,343	0,657	0,80	0,20	0,527	0,473
	0,40	0,60	0,059	0,941	0,40	0,60	0,205	0,792	0,70	0,30	0,412	0,588
	0,20	0,80	0,021	0,979	0,20	0,80	0,109	0,891	0,50	0,50	0,244	0,756
	0,10	0,90	0,011	0,989					0,30	0,70	0,129	0,871
0,4	0,90	0,10	0,305	0,695	0,90	0,10	0,622	0,378	0,95	0,05	0,806	0,194
	0,80	0,20	0,177	0,823	0,80	0,20	0,434	0,566	0,90	0,10	0,703	0,297
	0,60	0,40	0,071	0,929	0,60	0,40	0,236	0,764	0,80	0,20	0,539	0,461
	0,40	0,60	0,029	0,971	0,40	0,60	0,127	0,873	0,70	0,30	0,422	0,578
									0,50	0,50	0,251	0,749
									0,30	0,70	0,133	0,867
0,6	0,90	0,10	0,247	0,753								
	0,80	0,20	0,133	0,867								
	0,60	0,40	0,049	0,951								
	0,40	0,60	0,019	0,981								
	0,20	0,80	0,006	0,994								

Table 4.1 Equilibrium composition of both phases of binary systems, Amberlite 400, Na_2SO_4, $NaNO_3$; Na_2SO_4, NaCl and $NaNO_3$, NaCl for various total normalities of the solutions at 298°K.

Wilson parameters			equilibrium constant
Λ_{ij}	Cl	NO_3	
Cl	1,0	2,4627	$K^{NO_3}_{Cl} = 3,780$
NO_3	0,39121	1,0	



equilibrium quotient

mole fraction nitrate ion on resin

Figure 4.1 Variation of equilibrium quotient with nitrate ion mole fraction for binary system Amberlite 400, 0,2 N, 0,4 N mixture of NaCl and $NaNO_3$ at 298°K. Comparison of this work with published data. The solid line represents the least-squares fit of the experimental data with the Wilson parameters and equilibrium constant reported. Tabulated results in Appendix Table F.1

Wilson parameters			equilibrium constant
Λ_{ij}	SO_4	Cl	
SO_4	1,0	0,21192	$K^{Cl^*}_{SO_4}$ 5,104
Cl	3,7355	1,0	

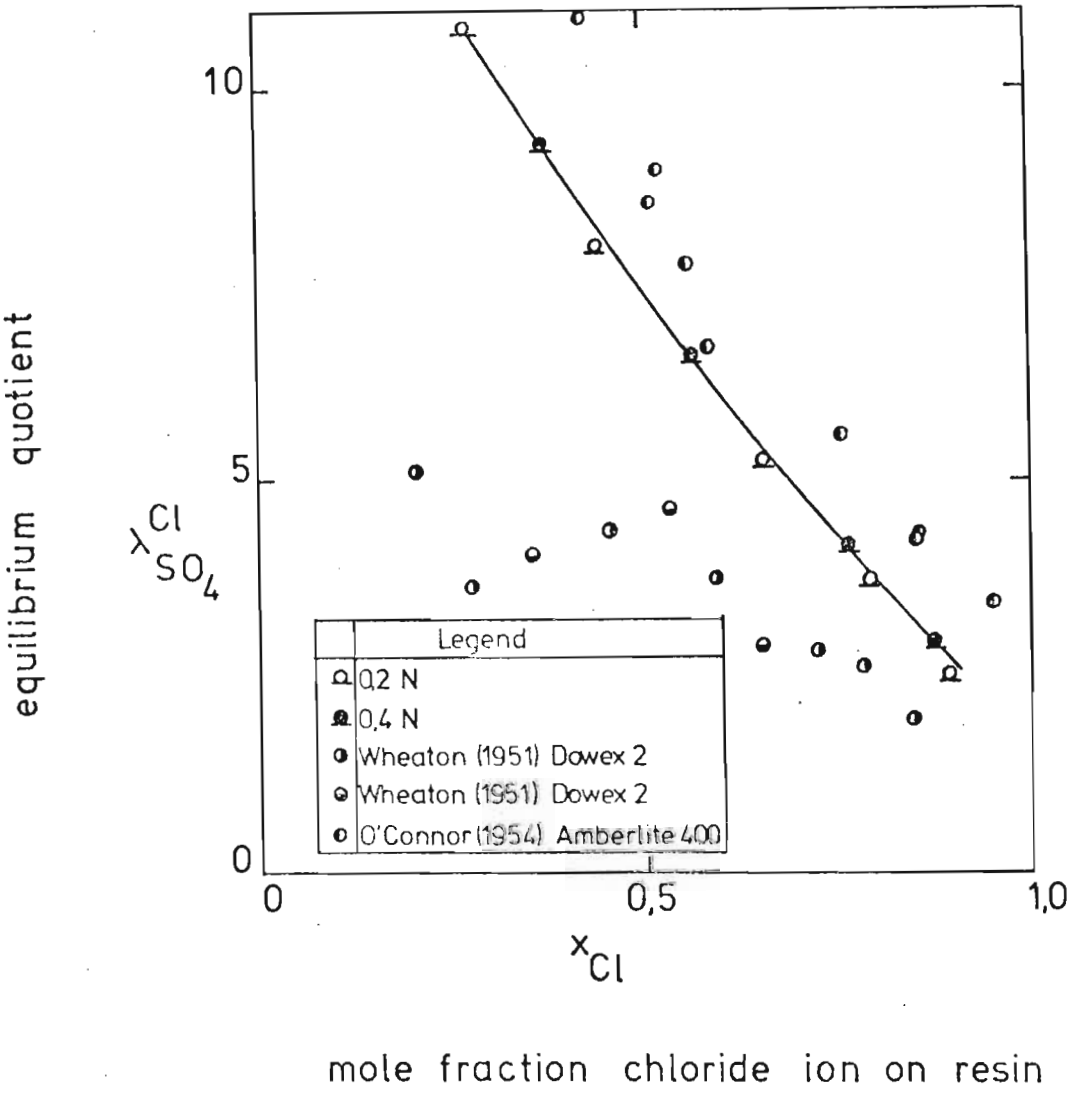


Figure 4.2 Variation of equilibrium quotient with chloride ion mole fraction for binary system Amberlit 400, 0,2 N, 0,4 N mixture of NaCl and Na_2SO_4 at 298°K. Comparison of this work with published data. The solid line represents the least-squares fit of the experimental data with the Wilson parameters and equilibrium constant reported. Tabulated results in Appendix Table F.2.

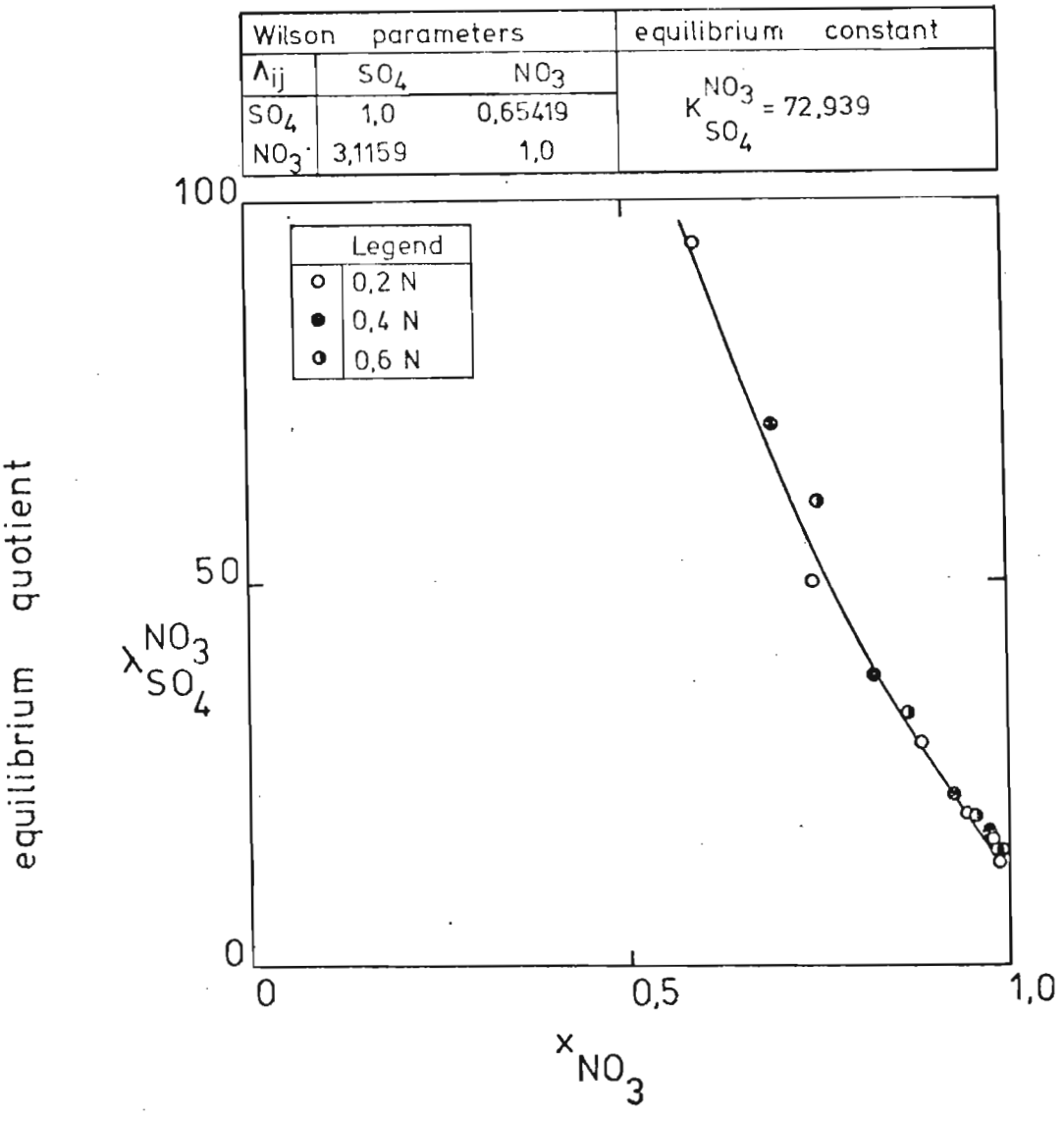


Figure 4.3 Variation of equilibrium quotient with nitrate ion mole fraction for binary system Amberlite 400, 0,2 N, 0,4 N, 0,6 N mixture of $NaNO_3$, Na_2SO_4 at 298°K. The solid line represents the least-squares fit of the experimental data with the Wilson parameters and equilibrium constant reported. Tabulated results in Appendix Table F.3.

strong base anion resin with the same cross-linkage the functional group of Dowex 2 is $-N(alkylol)(alkyl)_2^+$ compared to $-N(alkyl)_3^+$ for Amberlite 400.

It is noted that the equilibrium quotient, composition relationships at different normalities for this work and that of O'CONNOR (1954) and WHEATON and BAUMAN (1951) generate single curves within experimental error. This indicates that the activity coefficient calculations in the solution phase are sufficiently accurate. (DAVIDSON and ARGENSINGER, 1953).

Equilibrium data in the form of equilibrium quotients is applied to estimate the interaction coefficients of the Wilson equation and the thermodynamic equilibrium constants of the exchange reactions as outlined in Chapter 3.

Binary interaction coefficients obtained in Table 4.2 are seen to be reasonable numbers when compared to those generated by vapour-liquid equilibria. The fact that for each binary system investigated the one parameter exceeds unity while the other is less than unity indicates that the deviations from ideality are not large.

The estimates of the thermodynamic equilibrium constants are listed for each exchange reaction in Table 4.2. The three binary constants are related and hence we may infer for example $K_{SO_4}^{Cl^*}$ from $K_{SO_4}^{NO_3}$ and $K_{Cl}^{NO_3}$. In this case $K_{SO_4}^{Cl^*} = K_{SO_4}^{NO_3} / (K_{Cl}^{NO_3})^2 = 5{,}104$ which agrees within the error ascribed to the estimate of 5,094. This is evidence of the consistency of the experimental data employed. With the inferred value of $K_{SO_4}^{Cl^*}$ the Wilson parameters have been re-estimated. These parameters are subsequently used in calculations.

Ion Exchange Reaction	Parameters Estimated				R.M.S. Error
	Equilibrium Constant	Wilson Parameters			
$R_2SO_4 + 2NO_3 \rightleftarrows 2RNO_3 + SO_4$	$K_{SO_4}^{NO_3} = 72,939$	Λ_{ij}	SO_4	NO_3	± 5,8
		SO_4	1,0	0,65419	
		NO_3	3,1159	1,0	
$R_2SO_4 + 2Cl \rightleftarrows 2RCl + SO_4$	$K_{SO_4}^{Cl} = 5,094$	Λ_{ij}	SO_4	Cl	± 2,7
		SO_4	1,0	0,2280	
		Cl	3,674	1,0	
$RCl + NO_3 \rightleftarrows RNO_3 + Cl$	$K_{Cl}^{NO_3} = 3,780$	Λ_{ij}	Cl	NO_3	± 3,5
		Cl	1,0	2,4627	
		NO_3	0,39121	1,0	
$R_2SO_4 + 2Cl \rightleftarrows 2RCl + SO_4$	$K_{SO_4}^{*Cl} = 5,104$	Λ_{ij}	SO_4	Cl	± 2,7
		SO_4	1,0	0,21192	
		Cl	3,7355	1,0	
	$K_{SO_4}^{*Cl} = K_{SO_4}^{NO_3}/(K_{Cl}^{NO_3})^2$				

Table 4.2 Estimates of parameters, Equilibrium Constant and Wilson Parameters for binary systems. Root mean square error of the experimental and least squares fit of equilibrium quotients. Inferred equilibrium constant for SO_4^{2-} - Cl^- binary system at 298°K.

The agreement between the experimental and fitted equilibrium quotients obtained with the Wilson model is illustrated in Figures 4.4, 4.5 and 4.6. The corresponding root mean square error between fitted and experimental equilibrium quotients is less than ± 6% as reported in Table 4.2.

The variation of the equilibrium quotient with resin composition is shown as the best-fit curve through the experimental points in Figures 4.1, 4.2 and 4.3.

The agreement between the fitted and experimental resin phase compositions for the binary systems is good as shown in Figures 4.7, 4.8 and 4.9. As indicated earlier the scatter in the plot of fitted and experimental resin phase composition is significantly less than that for the fitted and experimental equilibrium quotients.

A specimen calculation of the fitted resin phase composition for the first solution condition in Table 4.1 is presented in the Appendix J.2.1.B.

For completeness the variation of the activity coefficients with composition have been determined from the Wilson equation over the entire composition range as shown in Figures 4.10, 4.11 and 4.12. It can be seen that in general the resin phase activity coefficient of the sulphate ion is the most sensitive to composition.

From the results presented it may be concluded that the non-idealities in the resin phase are well described by the Wilson model. The predictive power of this model is tested in the following section.

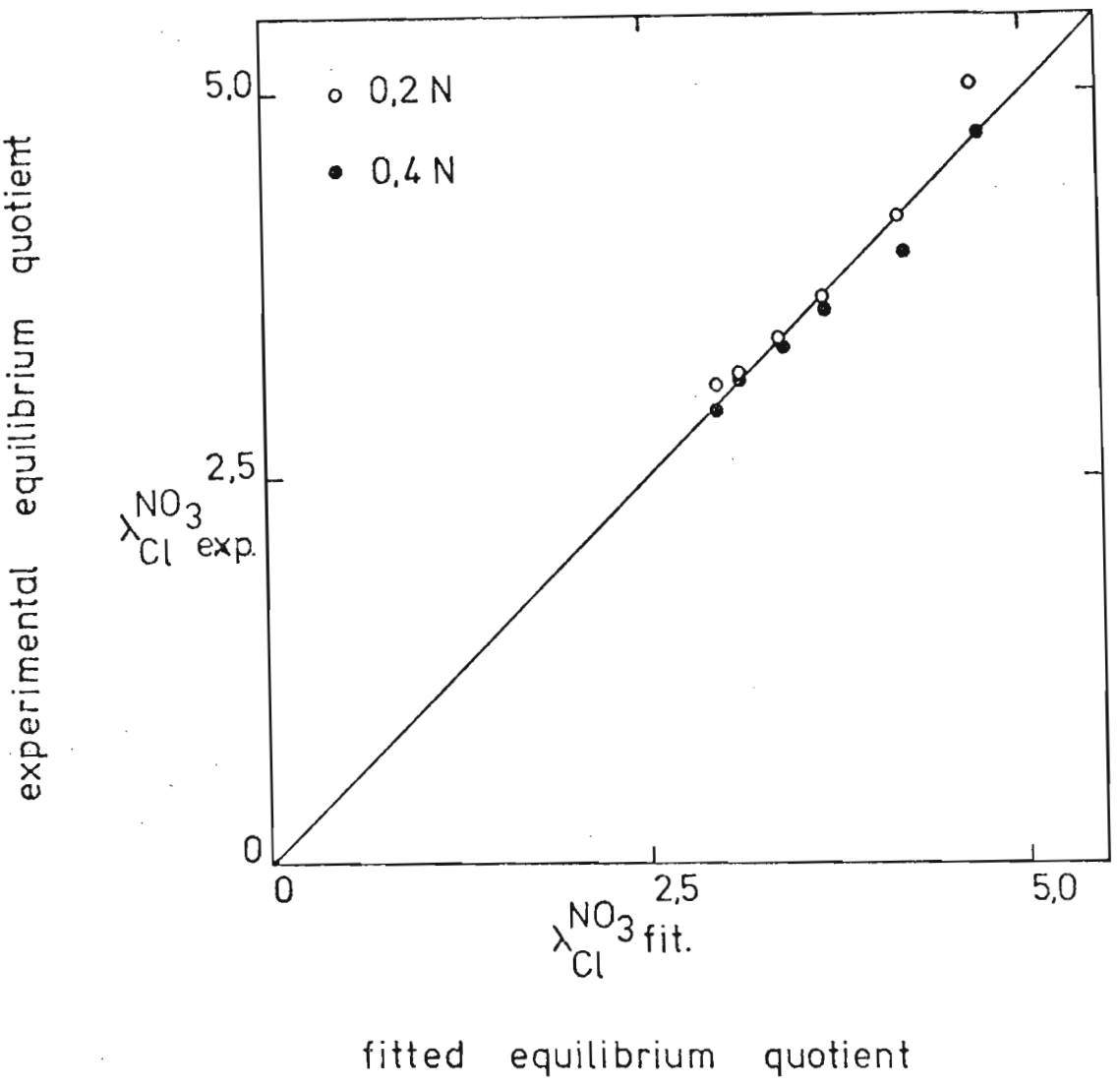


Figure 4.4 Comparison of fitted and experimental equilibrium quotient for binary system Amberlite 400, 0,2 N, 0,4 N mixture of NaCl, $NaNO_3$ at 298°K. Tabulated results in Appendix Table F.1.

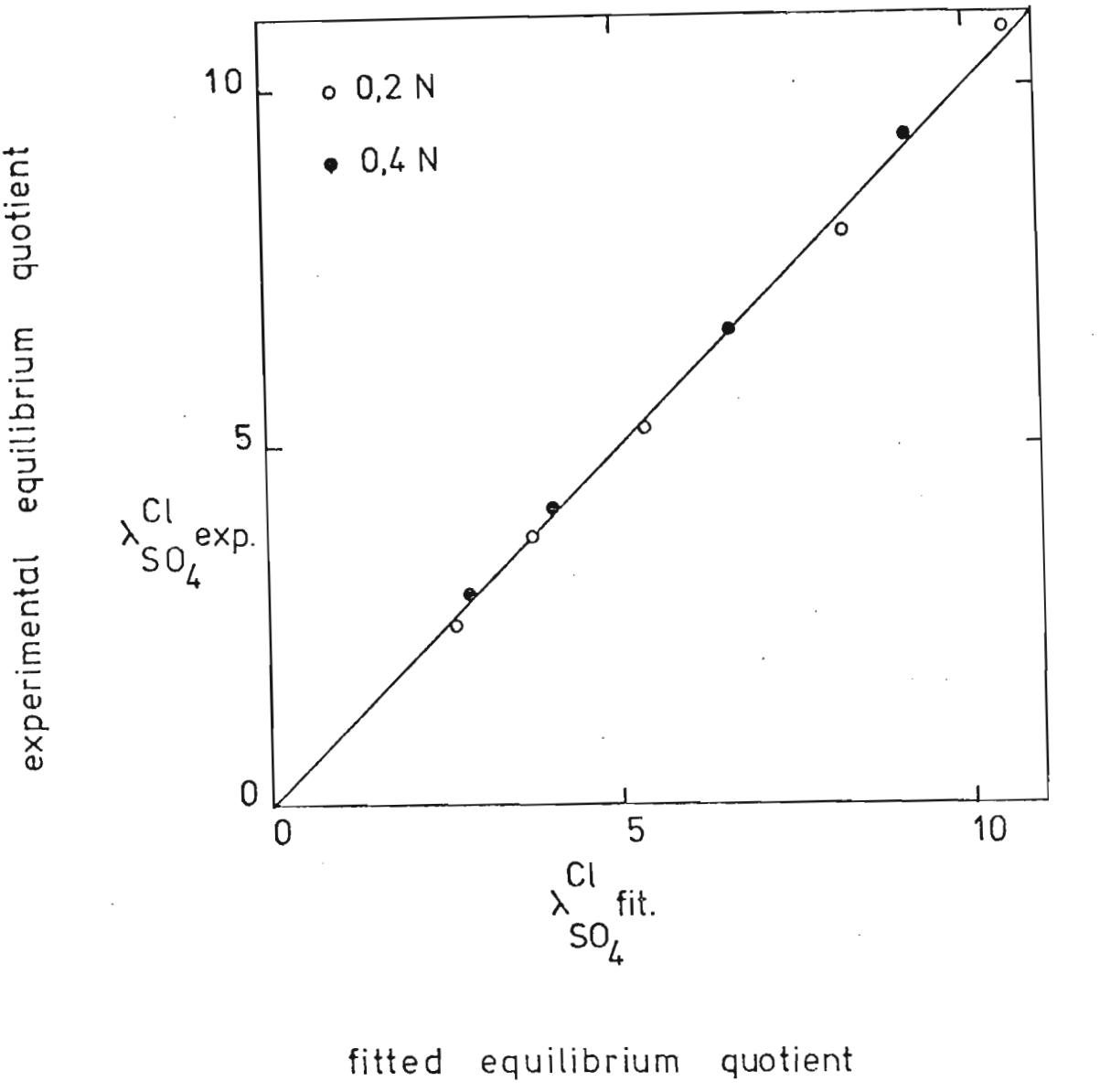


Figure 4.5 Comparison of fitted and experimental equilibrium quotient for binary system, Amberlite 400, 0,2 N, 0,4 N mixture of NaCl and Na_2SO_4 at 298°K. Tabulated results in Appendix Table F.2.

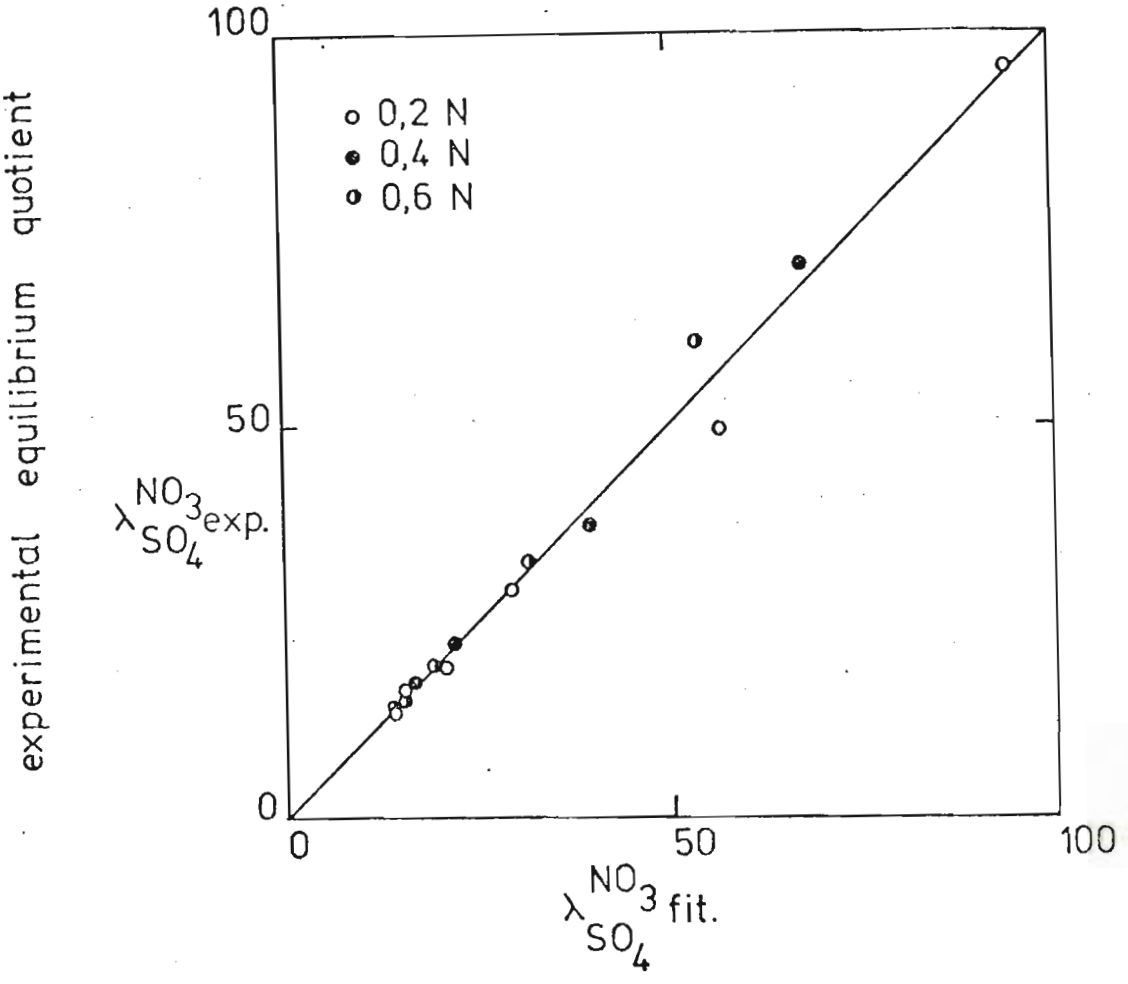


Figure 4.6 Comparison of fitted and experimental equilibrium quotient for the binary system, Amberlite 400, 0,2 N, 0,4 N, 0,6 N mixture of $NaNO_3$ and Na_2SO_4 at 298°K. Tabulated results in Appendix Table F.3.

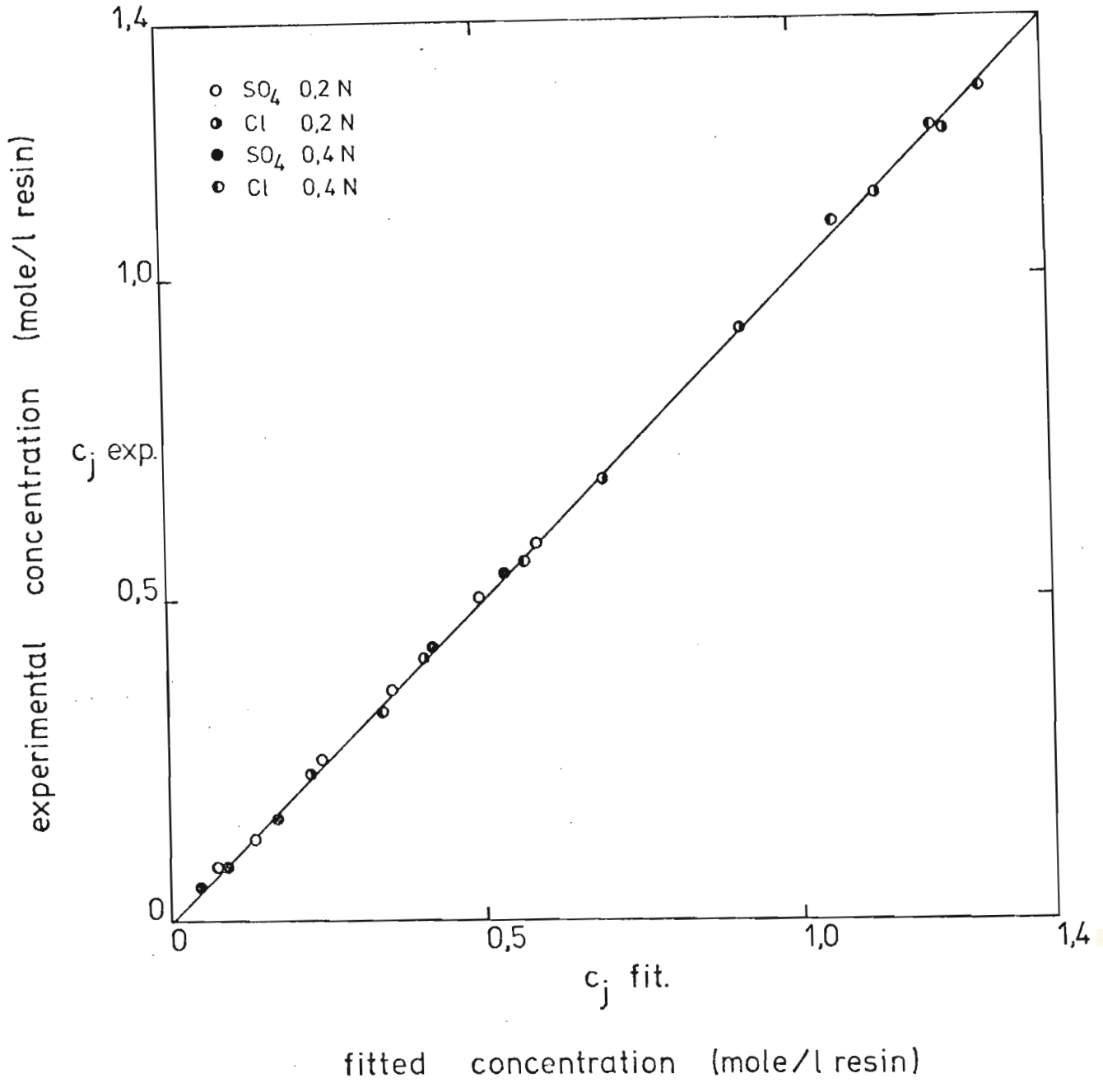


Figure 4.7 Comparison of fitted and experimental concentration on resin for binary system Amberlite 400, 0,2 N, 0,4 N mixture of NaCl and Na_2SO_4 at 298°K. Capacity is 1,4 equiv/l resin. Wilson parameters and equilibrium constants used are reported in Table 4.2. Tabulated data in Appendix Table F.4.

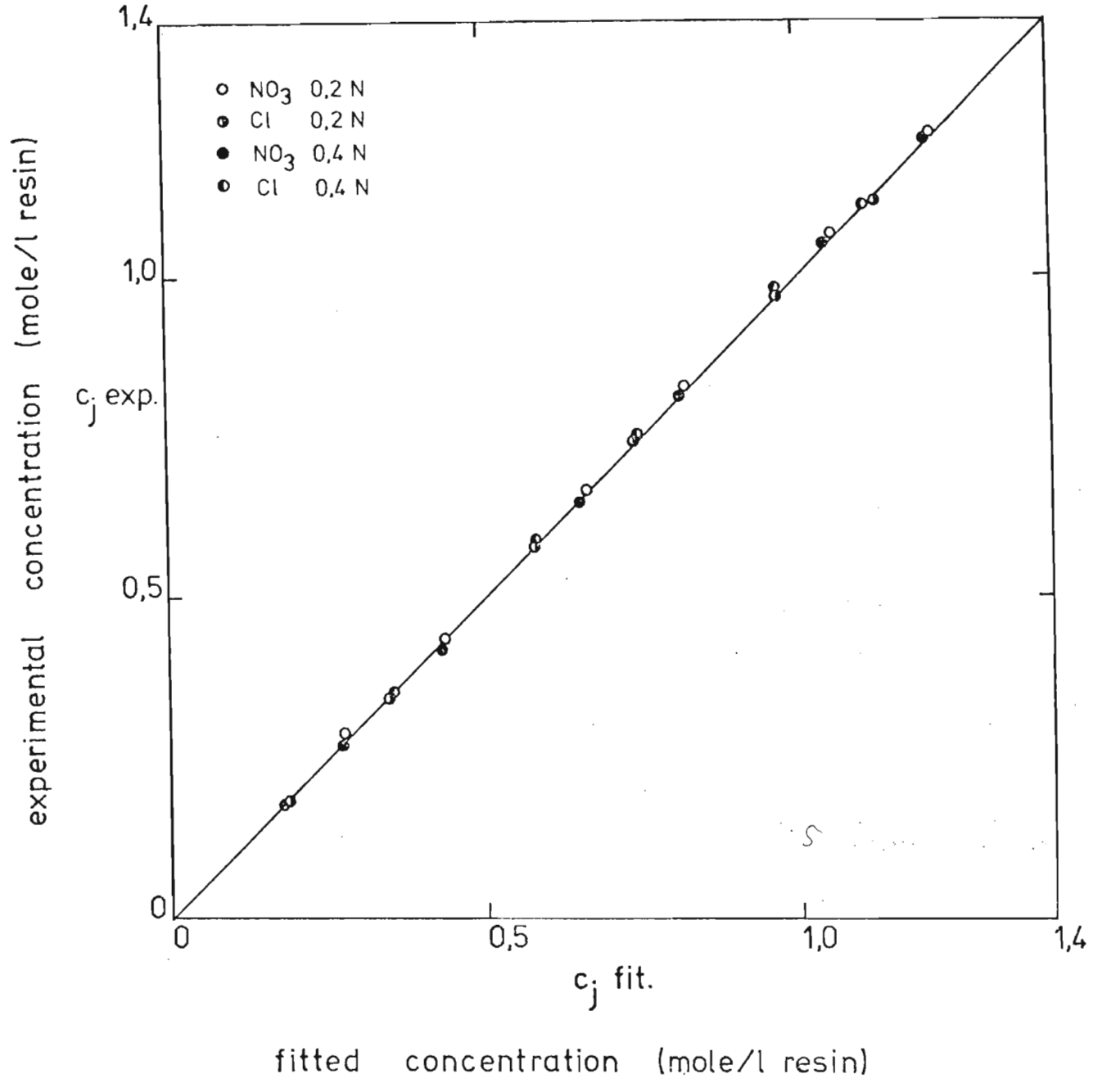


Figure 4.8 Comparison of fitted and experimental concentration on resin for the binary system Amberlite 400, 0,2 N and 0,4 N mixture of $NaNO_3$ and NaCl at 298°K. Capacity is 1,4 equiv./l resin. Wilson parameters and equilibrium constant used are reported in Table 4.2. Tabulated data in Appendix Table F.5.

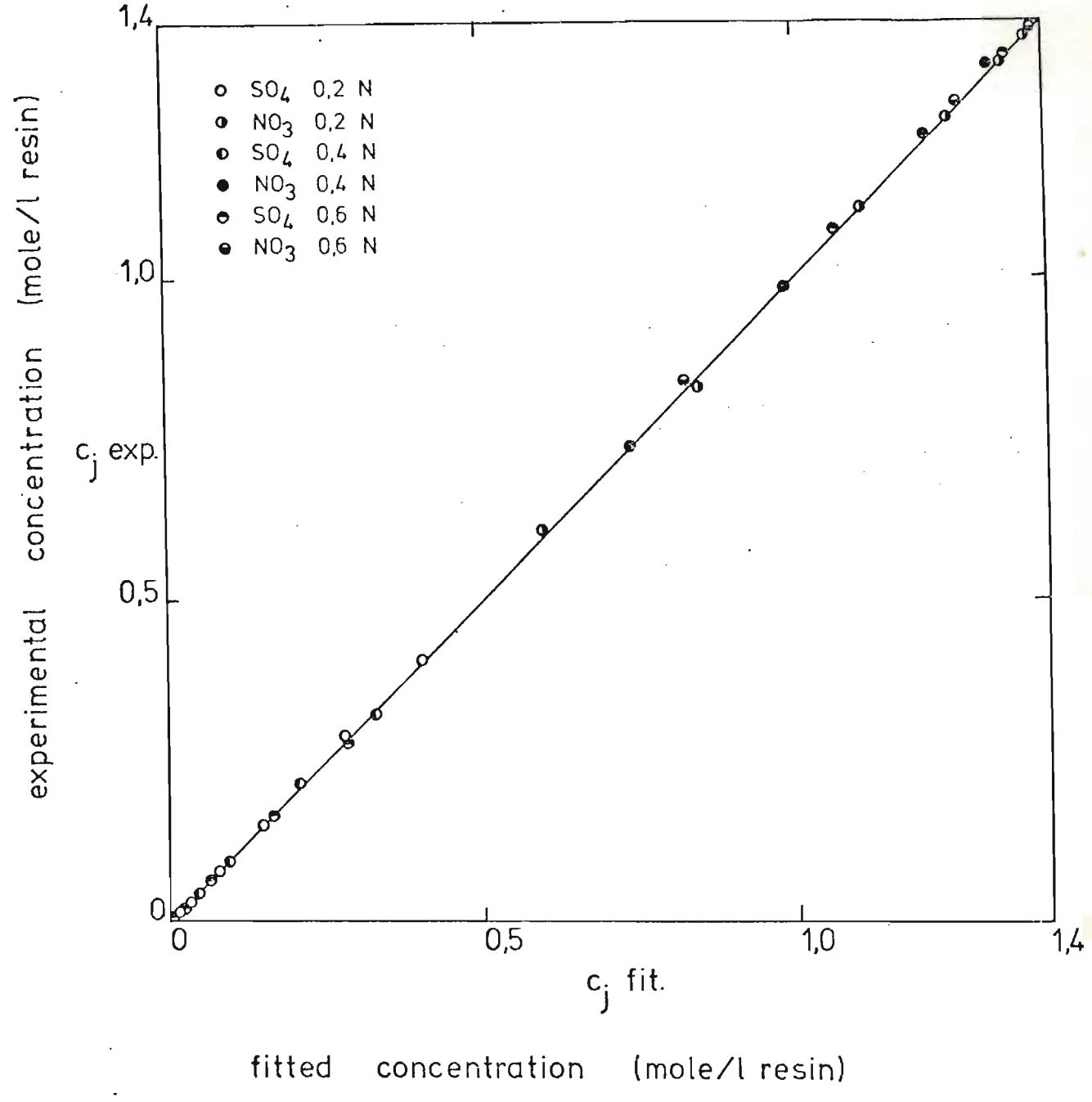


Figure 4.9 Comparison of fitted and experimental concentration on resin for binary system Amberlite 400, 0,2 N, 0,4 N, 0,6 N mixture of Na_2SO_4 and $NaNO_3$ at 298°K. Capacity is 1,4 equiv./l resin. Wilson parameters and equilibrium constant used are reported in Table 4.2. Tabulated results in Appendix Table F.6.

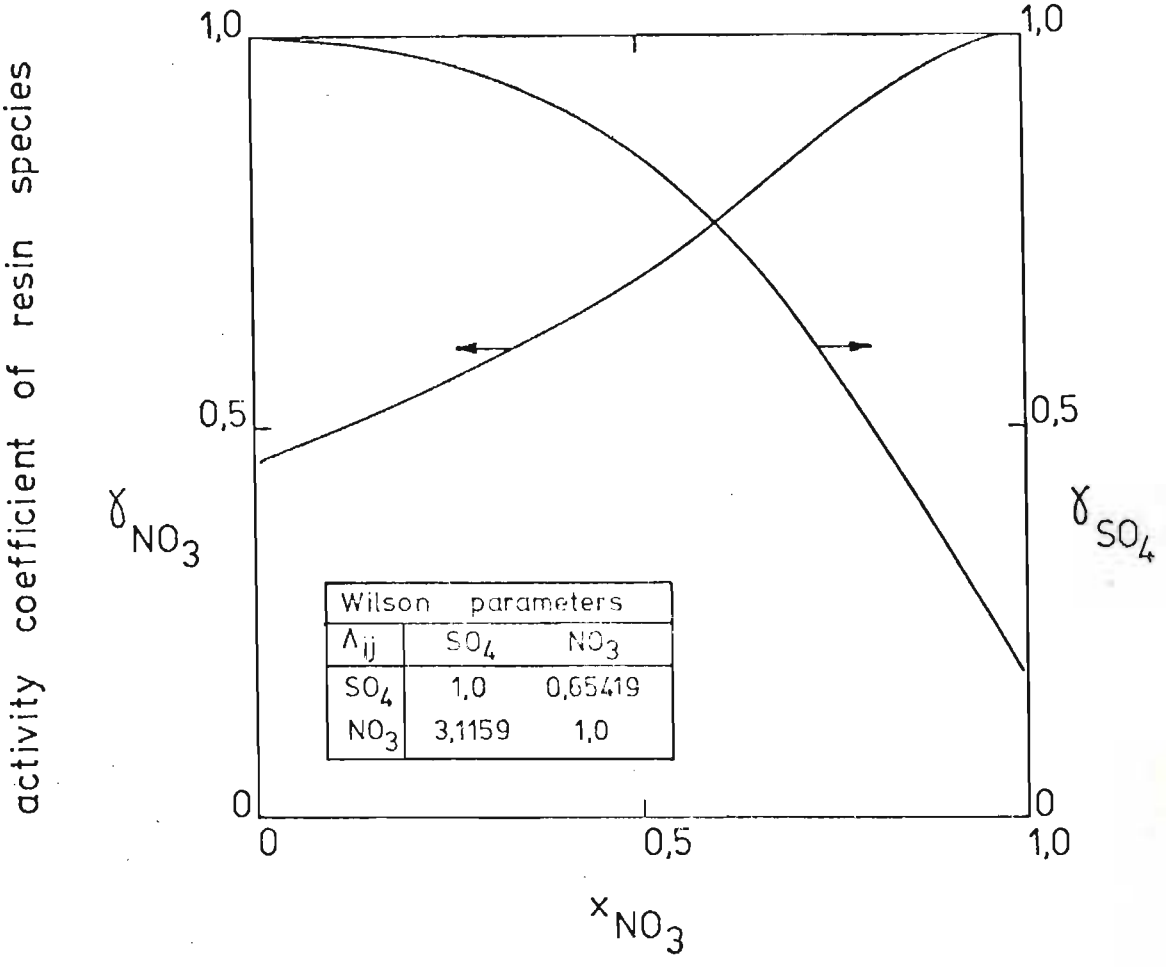


Figure 4.10 Variation of the activity coefficients of the resin species with nitrate ion mole fraction for the binary system Amberlite 400, mixture of $NaNO_3$ and Na_2SO_4 at 298°K.

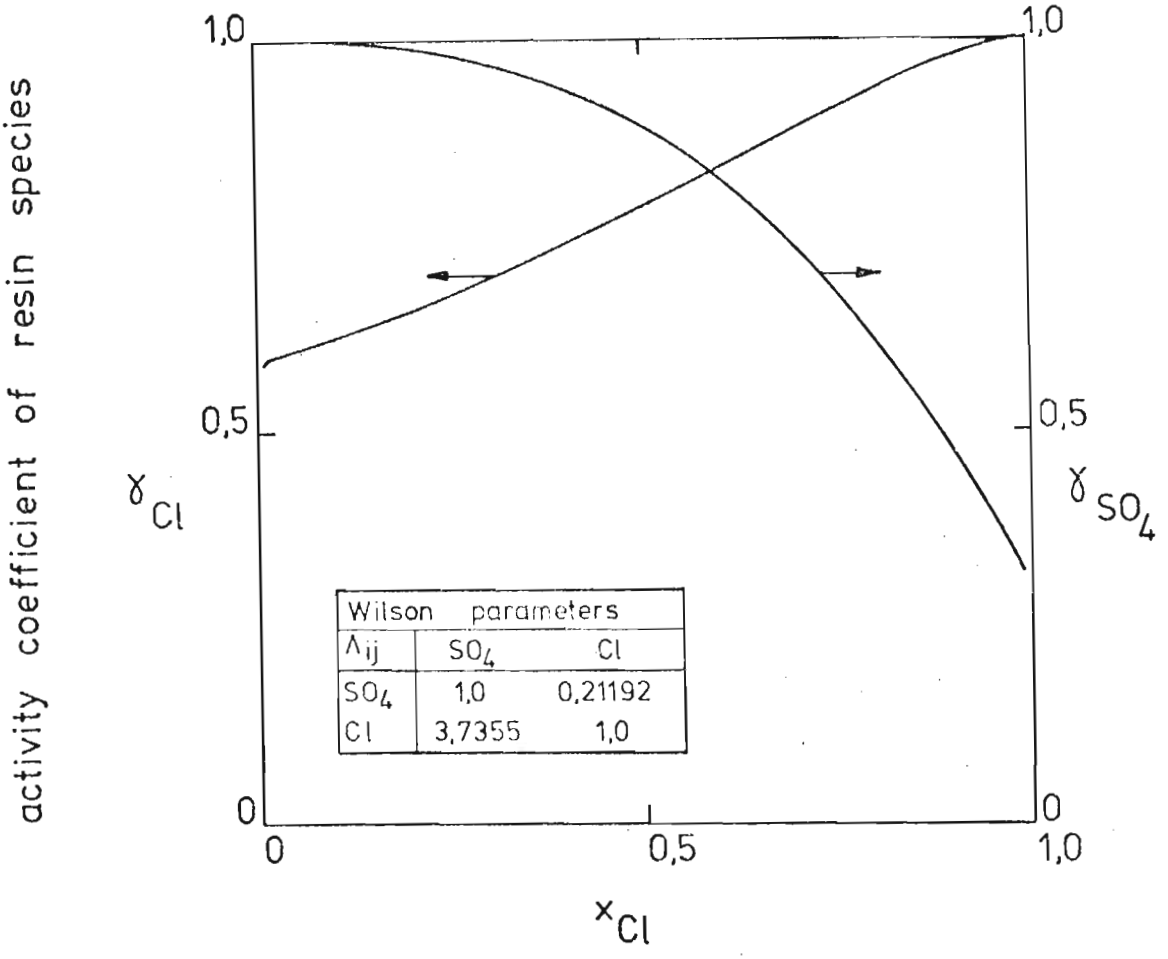
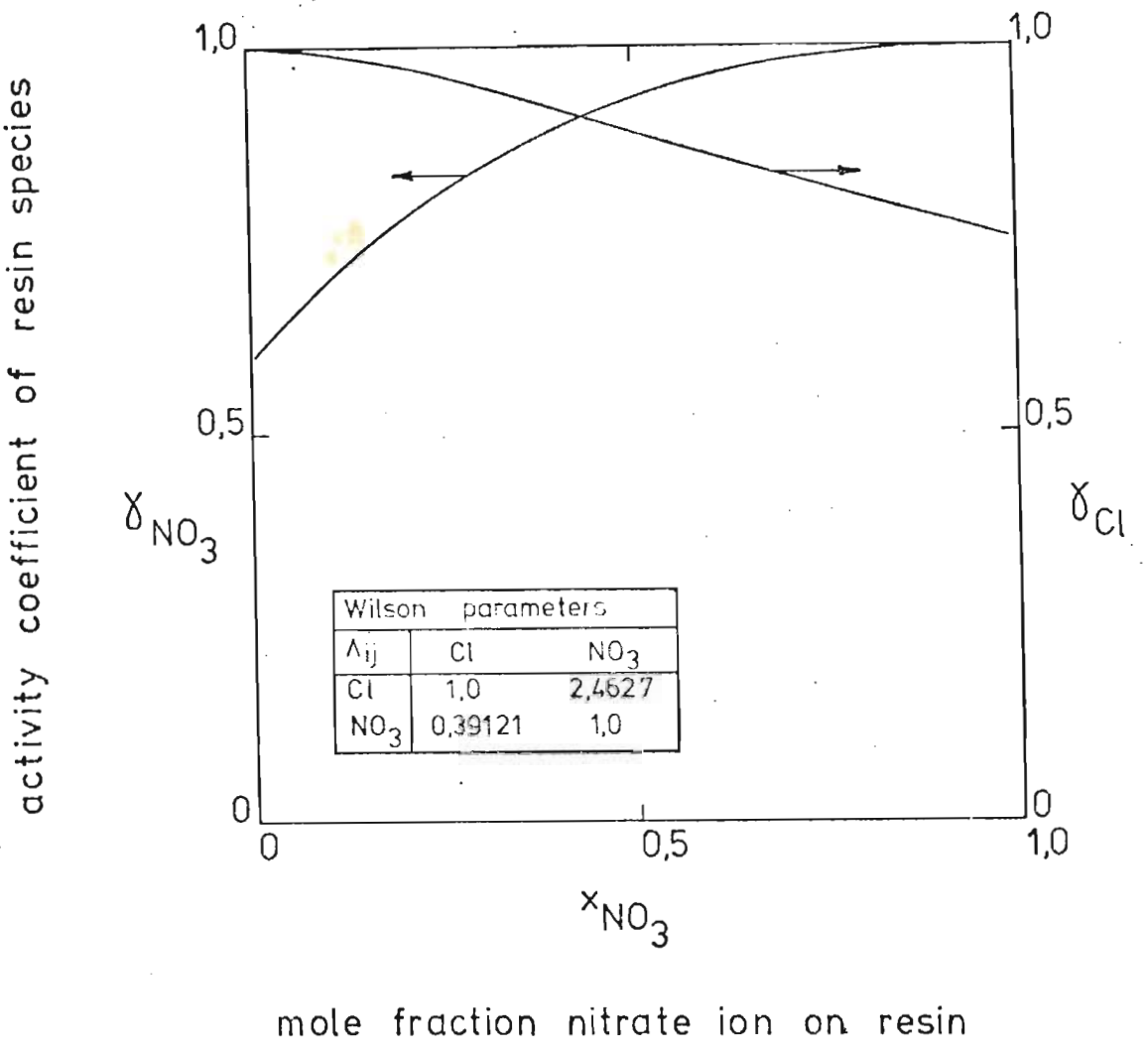


Figure 4.11 Variation of the activity coefficients of the resin species with chloride ion mole fraction for the binary system Amberlite 400, mixture of NaCl and Na_2SO_4 at 298°K.



Figre 4.12 Variation of the activity coefficients of the resin species with nitrate ion mole fraction for the binary system Amberlite 400, mixture of $NaNO_3$ and NaCl at $298^{o}K$.

4.2 PREDICTION OF THE TERNARY SYSTEM SO_4^{2-} - NO_3^- - Cl^-

The interaction parameters and the equilibrium constants estimated for the three binary systems alone, are combined through the Wilson equation to predict the equilibrium activity coefficients and composition in the resin phase for specified initial and solution conditions. The solution phase activities are first determined for the ions SO_4^{2-}, NO_3^-, Cl^-, Na^+ and $NaSO_4^-$ in the test solutions. The relevant activities and a specified volume of resin of known capacity and composition in this case $x_{SO_4} = 1,0$, are used to determine the equilibrium extents as outlined in Chapter 3 and hence the resin composition.

The independent heterogeneous equations required to solve this system are

$$R_2SO_4 + 2NO_3^- \rightleftarrows 2RNO_3 + SO_4^{2-}$$

$$R_2SO_4 + 2Cl^- \rightleftarrows 2RCl + SO_4^{2-} \qquad (4.14)$$

A single solution phase complex is formed in this system

$$Na^+ + SO_4^{2-} \rightleftarrows NaSO_4^- \qquad (4.15)$$

In the predictions a capacity of 1,4 equivalents per litre of free settled resin is assumed.

Specimen calculations of the activity of the solution species and the prediction of the resin phase composition are given in the

Appendices J.2.1.A and J.2.1.C respectively for the first experimental condition of Table 4.3.

4.2.1 Test experiments for comparison with the predictions for the ternary systems SO_4^{2-} - NO_3^- - Cl^-

Ion exchange equilibria are determined for the system Amberlite 400, 0,2 N mixture of Na_2SO_4, $NaNO_3$ and NaCl at 298^oK.

The equivalent balance equation for the ternary system is

$$2c_{SO_4} + c_{NO_3} + c_{Cl} = \text{Capacity} \qquad (4.16)$$

A. EXPERIMENTAL

An eluant is selected which allows the concentration of each of the three components to be measured. Initially, 2 litres of 0,1 M sodium carbonate was used. However the nitrate concentrations of the eluates determined according to the method in Appendix E.5 were consistently more than 10% lower than the corresponding predicted values while the chloride and sulphate analyses agreed very well with the predicted concentration. It was thought that the nitrate had not been completely eluted. In the following test 4 litres of this solution was passed through the resin sample. Similar results were obtained. A stronger eluate was employed, 2 litres of 0,1 N perchloric acid. Once again while the chloride and sulphate results agreed with the predicted concentrations the nitrate results were more than 10% lower than the predicted values.

Finally, the nitrate concentration was inferred from the equivalent balance Equation (4.16)

$$c_{NO_3} = \text{Capacity} - 2c_{SO_4} - c_{Cl}$$

4.2.2 Results and discussion

For the solution conditions specified in Table 4.3 the predicted and experimental resin compositions are consistent over a large composition range. The predicted activity coefficients of the resinates for the corresponding ternary points are included in Table 4.3.

The agreement between the experimental and predicted resin phase compositions is within ± 5% as illustrated in Figure 4.13.

The final three results in Table 4.3 for solution conditions $y'_{SO_4} = 0,5$, $y'_{NO_3} = 0,1$ and $y'_{Cl} = 0,4$ have been performed in triplicate. The experimental results show a high degree of reproducibility.

Predictions have been made of the resin phase composition expressed in equivalent fractions for the entire solution composition range at 0,2 N and presented graphically on a ternary diagram according to STREAT and BRIGNAL (1970) as shown in Figure 4.14.

The equidistant axes refer to the equivalent fractions of species in the resin phase. Superimposed on these axes are contour lines which refer to the equivalent fraction of species in the solution phase. Ternary experimental data is identified on the ternary diagram. The results justify the extension of this approach to more complex systems.

Test No.	Equiv. Fraction in Solution			Equiv. Fraction in Resin Predicted			Equiv. Fraction in Resin Experimental			Activitity Coeff. in Resin Predicted		
	ΣSO_4	NO_3	Cl	SO_4	NO_3	Cl	SO_4	NO_3^*	Cl	SO_4	NO_3	Cl
1	0,20	0,10	0,70	0,128	0,318	0,554	0,104	0,332	0,564	0,387	0,849	0,926
2	0,40	0,10	0,50	0,234	0,336	0,430	0,218	0,353	0,429	0,495	0,840	0,892
17	0,50	0,05	0,45	0,332	0,218	0,450	0,322	0,235	0,443	0,621	0,751	0,890
4	0,60	0,10	0,30	0,347	0,363	0,290	0,352	0,375	0,273	0,600	0,823	0,842
5	0,70	0,10	0,20	0,413	0,380	0,207	0,412	0,396	0,192	0,653	0,810	0,810
6	0,80	0,10	0,10	0,487	0,401	0,112	0,480	0,419	0,101	0,705	0,790	0,771
7	0,10	0,50	0,40	0,033	0,764	0,203	0,029	0,771	0,200	0,228	0,989	0,806
8	0,20	0,40	0,40	0,073	0,700	0,227	0,070	0,706	0,224	0,268	0,978	0,819
9	0,30	0,30	0,40	0,123	0,619	0,258	0,126	0,620	0,254	0,325	0,958	0,834
10	0,40	0,20	0,40	0,190	0,511	0,299	0,190	0,517	0,293	0,410	0,918	0,851
18	0,60	0,20	0,20	0,284	0,549	0,167	0,278	0,564	0,159	0,487	0,903	0,809
12	0,55	0,05	0,40	0,365	0,222	0,413	0,346	0,253	0,401	0,652	0,746	0,875
13	0,50	0,40	0,10	0,174	0,761	0,064	0,175	0,760	0,065	0,342	0,968	0,779
14	0,50	0,30	0,20	0,201	0,658	0,141	0,207	0,656	0,137	0,386	0,949	0,803
15	0,50	0,20	0,30	0,236	0,528	0,236	0,250	0,522	0,228	0,449	0,912	0,832
16	0,50	0,10	0,40	0,289	0,348	0,363	0,289	0,357	0,354	0,548	0,833	0,869
3	0,50	0,10	0,40	0,289	0,348	0,363	0,280	0,368	0,352	0,548	0,833	0,869
11	0,50	0,10	0,40	0,289	0,348	0,363	0,291	0,354	0,355	0,548	0,833	0,869

Table 4.3 Comparison of experimental and predicted equilibrium composition of the ternary system Amberlite 400, 0,2 N mixture of Na_2SO_4, $NaNO_3$ and NaCl at 298°K. Predicted activity coefficients of resin species. Capacity is 1,4 equiv./l resin. This data is presented graphically in Figure 4.13.

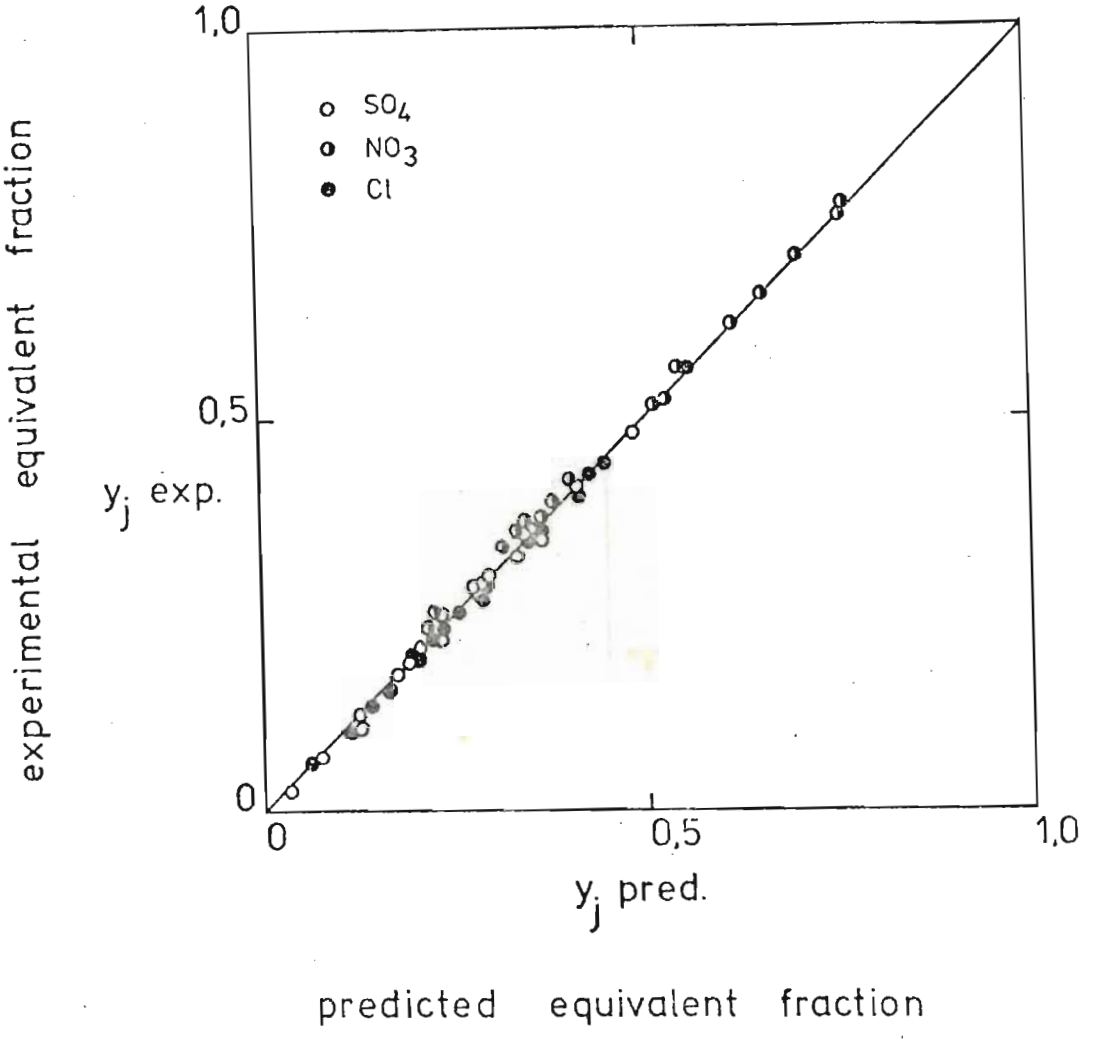


Figure 4.13 Comparison of predicted and experimental resin phase equivalent fraction for ternary system Amberlite 400, 0,2 N mixture of NaCl, $NaNO_3$ and Na_2SO_4 at 298°K based on experimental data of the binary systems. Capacity is 1,4 equiv./l resin. Tabulated results in Table 4.3.

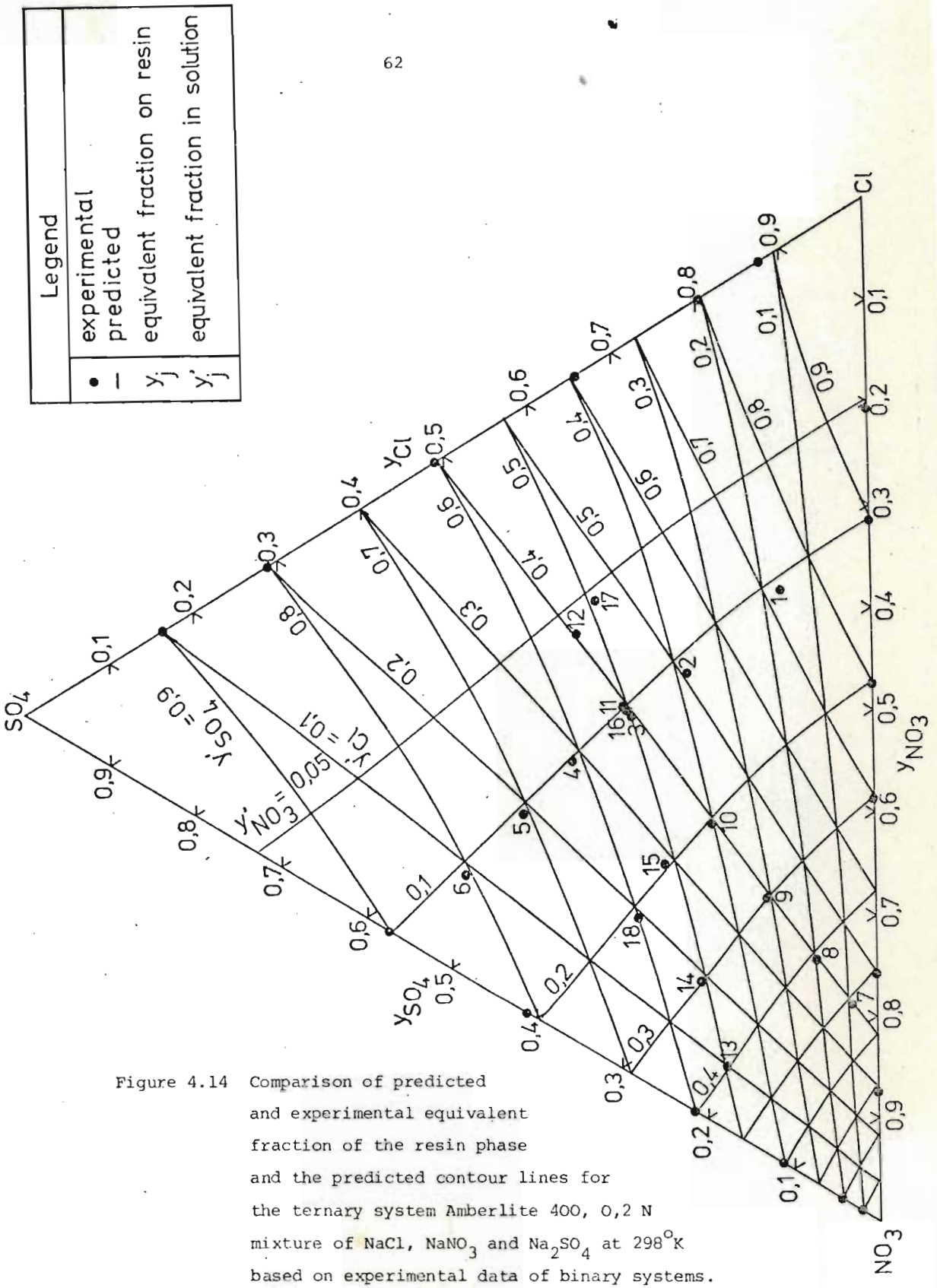


Figure 4.14 Comparison of predicted and experimental equivalent fraction of the resin phase and the predicted contour lines for the ternary system Amberlite 400, 0,2 N mixture of NaCl, $NaNO_3$ and Na_2SO_4 at 298°K based on experimental data of binary systems. Capacity is 1,4 equiv./l resin.

CHAPTER FIVE

INVESTIGATION OF TERNARY AND QUATERNARY SYSTEMS

Sulphuric acid is a major component in the leach liquors fed to ion exchange columns. Introducing this acid to the systems containing sulphate ions discussed in Chapter 4 results in complex formation of the bisulphate ion in both phases.

Generation of this complex in the solution and resin phases complicates the approach in that the binary systems NO_3^- - HSO_4^- and Cl^- - HSO_4^- are not feasible and hence it is not possible to predict the quarternary system SO_4^{2-} - HSO_4^- - NO_3^- - Cl^- from binary data alone. It is necessary to increase the order of the subsystems to ternary and perform experiments for the systems NO_3^- - SO_4^{2-} - HSO_4^- and Cl^- - SO_4^{2-} - HSO_4^-. However the binary SO_4^{2-} - HSO_4^- is measurable and the parameters obtained may be used in the characterisation of the ternary systems to reduce the number of parameters to be determined.

Similarly the parameters for the binary systems discussed previously are used in the characterisation of these ternary systems to further reduce the number of unknown parameters.

5.1 CHARACTERISATION EXPERIMENTS

5.1.1 Characterisation of the binary system SO_4^{2-} - HSO_4^-

Ion exchange equilibria are determined for the system Amberlite 400, mixture of Na_2SO_4 and H_2SO_4 at 298^{o}K.

The equilibria reaction for this system is represented by

$$R_2SO_4 + 2HSO_4^- \rightleftarrows 2RHSO_4 + SO_4^{2-} \tag{5.1}$$

and the corresponding equilibrium constant is

$$K^{HSO_4}_{SO_4} = \frac{a^2_{HSO_4}\ a'_{SO_4}}{a_{SO_4}\ a'^{\,2}_{HSO_4}} \tag{5.2}$$

The expression for the equilibrium quotient is

$$\lambda^{HSO_4}_{SO_4} = \frac{x^2_{HSO_4}\ a'_{SO_4}}{x_{SO_4}\ a'^{\,2}_{HSO_4}} \tag{5.3}$$

The equivalent balance equation for the exchanger phase at equilibrium is

$$2c_{SO_4} + c_{HSO_4} = \text{Capacity} \tag{5.4}$$

A mass balance equation for sulphate in the exchanger phase is

$$c_{SO_4} + c_{HSO_4} = c_{\Sigma SO_4} \tag{5.5}$$

Two complex reactions occur in the aqueous phase for this system

$$H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$$

$$Na^+ + SO_4^{2-} \rightleftarrows NaSO_4^- \tag{5.6}$$

An assumption made that the weak complex $NaSO_4^-$ is not absorbed by the resin is checked with this data. Combining Equation (5.4) and (5.5) the following is obtained

$$c_{HSO_4} = 2c_{\Sigma SO_4} - \text{Capacity} \qquad (5.7)$$

The three quantities in Equation (5.7) have been measured, this allows the directly measured bisulphate ion concentration c_{HSO_4} to be compared with $c^*_{HSO_4}$ as inferred from Equation (5.7).

A. EXPERIMENTAL

The elution solution for this system is 1N NaCl. The bisulphate concentration on the resin is determined from the titration of the eluate with standard base as outlined in Appendix E.4. Total sulphate in the eluate is determined according to the method described in Appendix E.2. The capacity is determined prior to the equilibrium as described in Appendix C.8.

B. RESULTS AND DISCUSSION

The experimental equilibrium composition of the resin and solution phases are summarised in Table 5.1 for the binary system SO_4^{2-} - HSO_4^-.

A check on the resin phase mass balance is possible with this data, the bisulphate ion concentration is inferred from the capacity and total sulphate on the resin, Equation (5.7) and compared with the measured bisulphate ion concentration in Table 5.1. The agreement is generally good. These results indicate that the $NaSO_4^-$ anion is not absorbed. The first six

Solution Phase (M)			Resin Phase (Mole/ℓ Resin)			
ΣSO_4	H	Na	Capacity	ΣSO_4	HSO_4	HSO_4*
0,3641	0,0593	0,6689	1,410	0,8961	0,370	0,382
0,3641	0,0593	0,6689	1,418	0,9047	0,374	0,391
0,3641	0,0593	0,6689	1,416	0,9081	0,374	0,400
0,3619	0,1866	0,5373	1,388	1,0606	0,688	0,733
0,3619	0,1866	0,5373	1,402	1,0692	0,704	0,736
0,3619	0,1866	0,5373	1,410	1,0675	0,696	0,725
0,4988	0,2775	0,7201	1,394	1,1137	0,8260	0,833
0,4706	0,2213	0,7200	1,363	1,0683	0,7376	0,774
0,4538	0,1875	0,7201	1,389	1,0400	0,6968	0,691
0,4373	0,1547	0,7200	1,396	1,0161	0,6412	0,636
0,4209	0,1219	0,7200	1,395	0,9878	0,5740	0,581
0,4045	0,0891	0,7200	1,388	0,9218	0,4564	0,456
0,4638	0,4180	0,5000	1,371	1,1703	0,9630	0,969
0,3981	0,2978	0,5000	1,381	1,1180	0,8625	0,845
0,2650	0,0290	0,5000	1,381	0,8070	0,2396	0,233
0,2613	0,0212	0,5000	1,361	0,7985	0,1870	0,236
0,2575	0,0153	0,5000	1,360	0,7573	0,1430	0,155
0,2538	0,0087	0,5000	1,371	0,7256	0,0870	0,080

Table 5.1 Equilibrium composition of solution and resin phases for binary system Amberlite 400, mixtures of Na_2SO_4 and H_2SO_4 at 298°K. Mass balance check for resin phase.

results in Table 5.1 are for two conditions in triplicate which indicate good reproducibility.

The sulphate ion concentration in the resin is not measurable directly, in this case it is inferred from the capacity and bisulphate ion concentration, Equation (5.4).

Equilibrium quotients have been determined for each equilibrium condition. The variation of the equilibrium quotient with composition in the resin phase is presented in Figure 5.1. It can be seen that this work is entirely consistent with the published data of ANDERSON *et al* (1955). At bisulphate mole fractions above 0,6 agreement with the published data of O'CONNOR (1954) and NELSON and KRAUS (1958) is reasonable.

Although the resin employed by NELSON and KRAUS (1958) was Dowex 1, the cross-linkage was 10% DVB compared with 8% for this sample. The date of ANDERSON *et al* (1955) was obtained with a sample of Dowex 1 of 8% DVB which is equivalent to this sample of Amberlite 400. The consistency of the two sets of data suggests that the parameters obtained are not limited to the sample of resin characterised.

Binary interaction coefficients and the thermodynamic equilibrium constant have been estimated from the experimental data in the form of equilibrium quotients. The parameters are presented in Figure 5.1. The agreement between experimental and fitted equilibrium quotients obtained applying these parameters in the Wilson model is illustrated in Figure 5.2. The root mean square error is less than ± 7%.

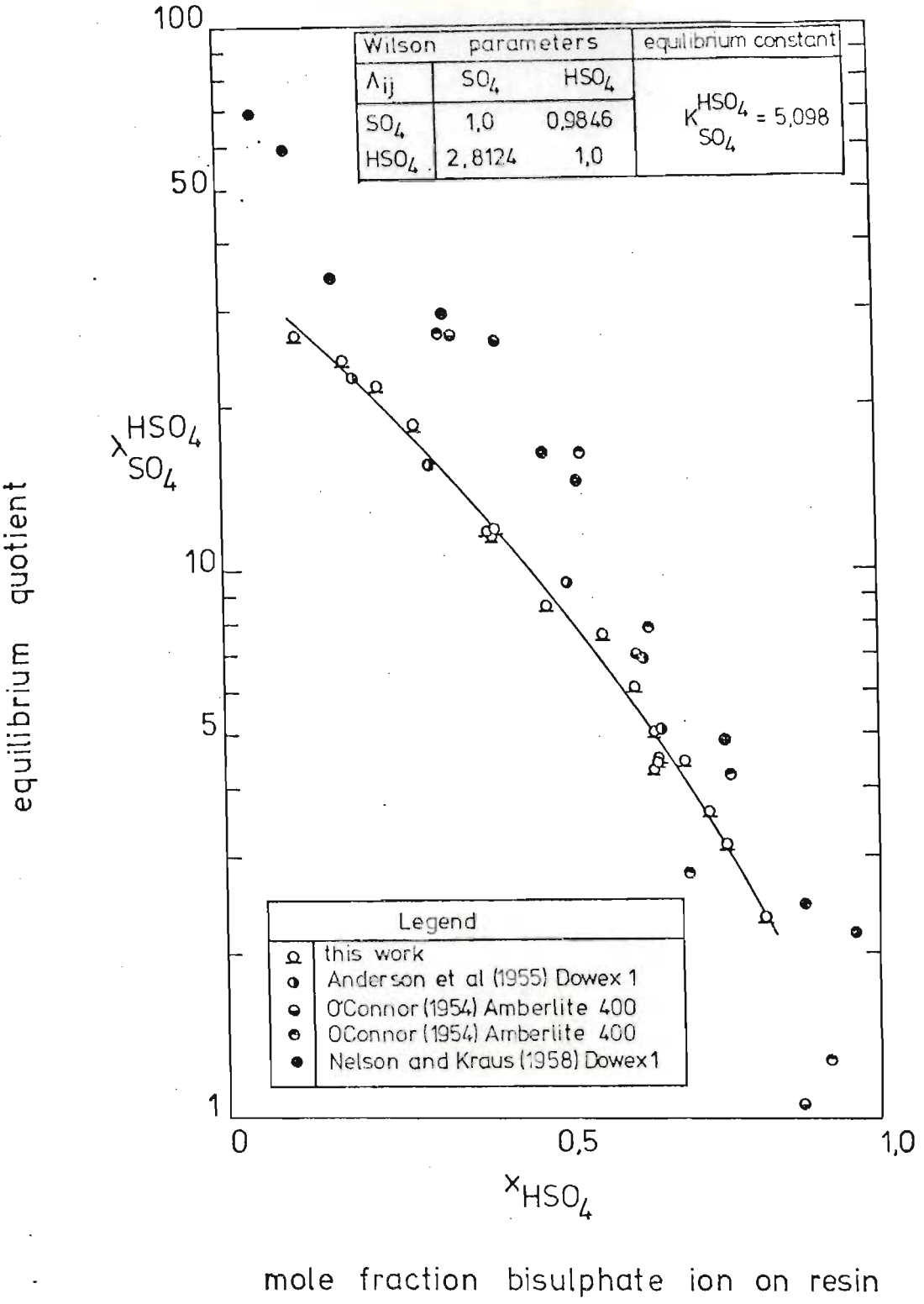


Figure 5.1 Variation of the equilibrium quotient with bisulphate ion mole fraction for binary system Amberlite 400, mixture of H_2SO_4 and Na_2SO_4 at 298°K. Comparison of this work with published data. The solid line represents the least-squares fit of experimental data with the Wilson parameters and equilibrium constant reported. Tabulated results in Appendix Table F.7.

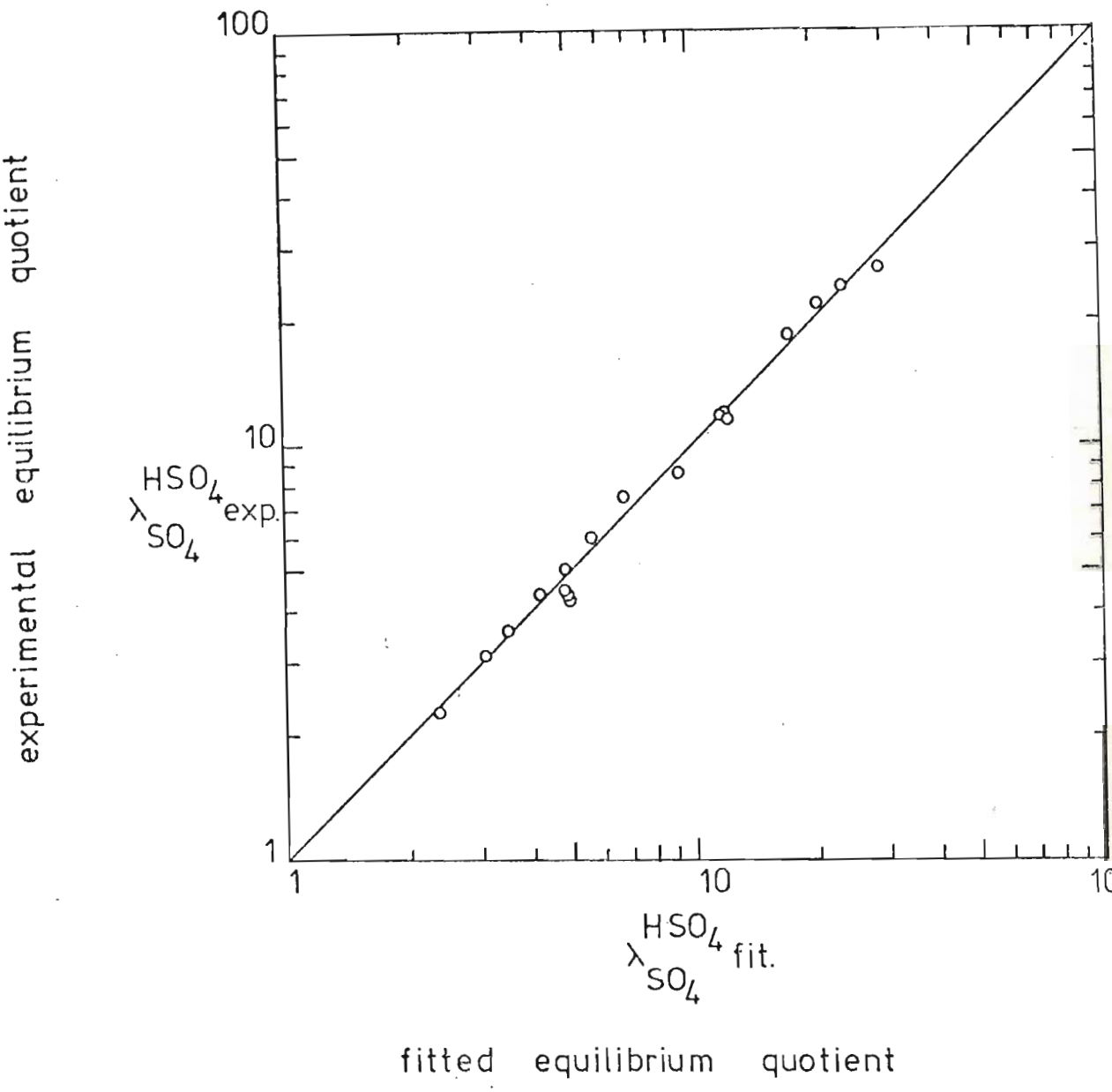


Figure 5.2 Comparison of fitted and experimental equilibrium quotients for the binary system Amberlite 400, mixture of Na_2SO_4 and H_2SO_4 at 298°K. Tabulated results in Appendix Table F.7.

The fitted relationship between the equilibrium quotient and resin composition is shown as the best fit curve through the experimental points of Figure 5.1.

The variation of activity coefficients with composition have been determined from the Wilson equation over the entire composition range as illustrated in Figure 5.3.

The fitted composition data of the binary system for the solution conditions specified in Table 5.1 compared with the experimental data in Figure 5.4 indicates the lower sensitivity of the composition variables with respect to the equilibrium quotients.

A specimen calculation of the fitted resin phase composition for the first solution condition in Table 5.1 is presented in Appendix J.2.1.B.

The SO_4^{2-} - HSO_4^- binary system is well characterised with the Wilson model.

5.1.2 Characterisation of the ternary system SO_4^{2-} - HSO_4^- - Cl^-

The ion exchange equilibria are determined for the system Amberlite 400, mixture of Na_2SO_4, NaCl and H_2SO_4 at 298°K.

The equilibrium reactions for this system are

$$R_2SO_4 + 2HSO_4^- \rightleftarrows 2RHSO_4 + SO_4^{2-}$$

$$R_2SO_4 + 2Cl^- \rightleftarrows 2RCl + SO_4^{2-} \qquad (5.8)$$

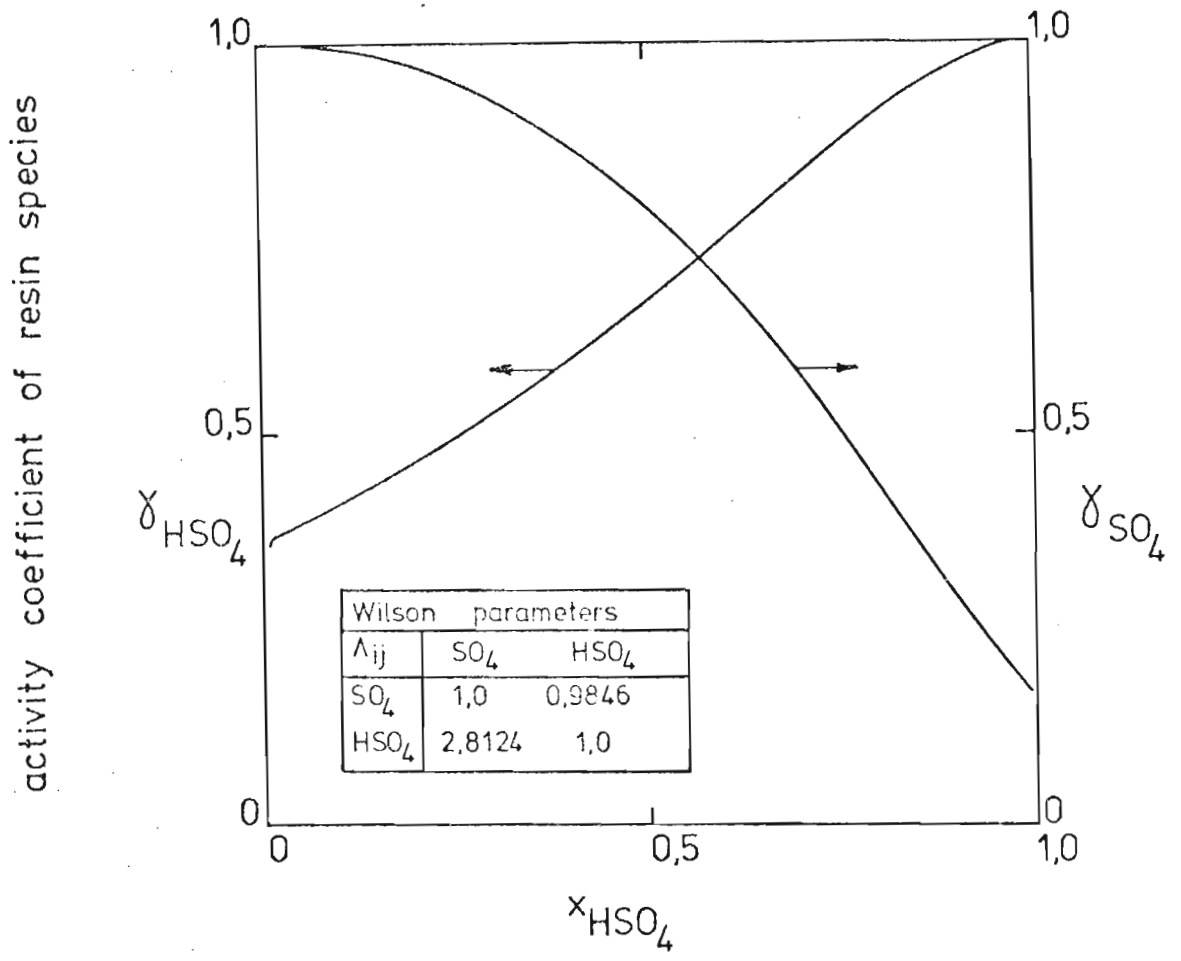


Figure 5.3 Variation of activity coefficients of resin species with bisulphate ion mole fraction for binary system Amberlite 400, mixture of Na_2SO_4 and H_2SO_4 at $298^{o}K$.

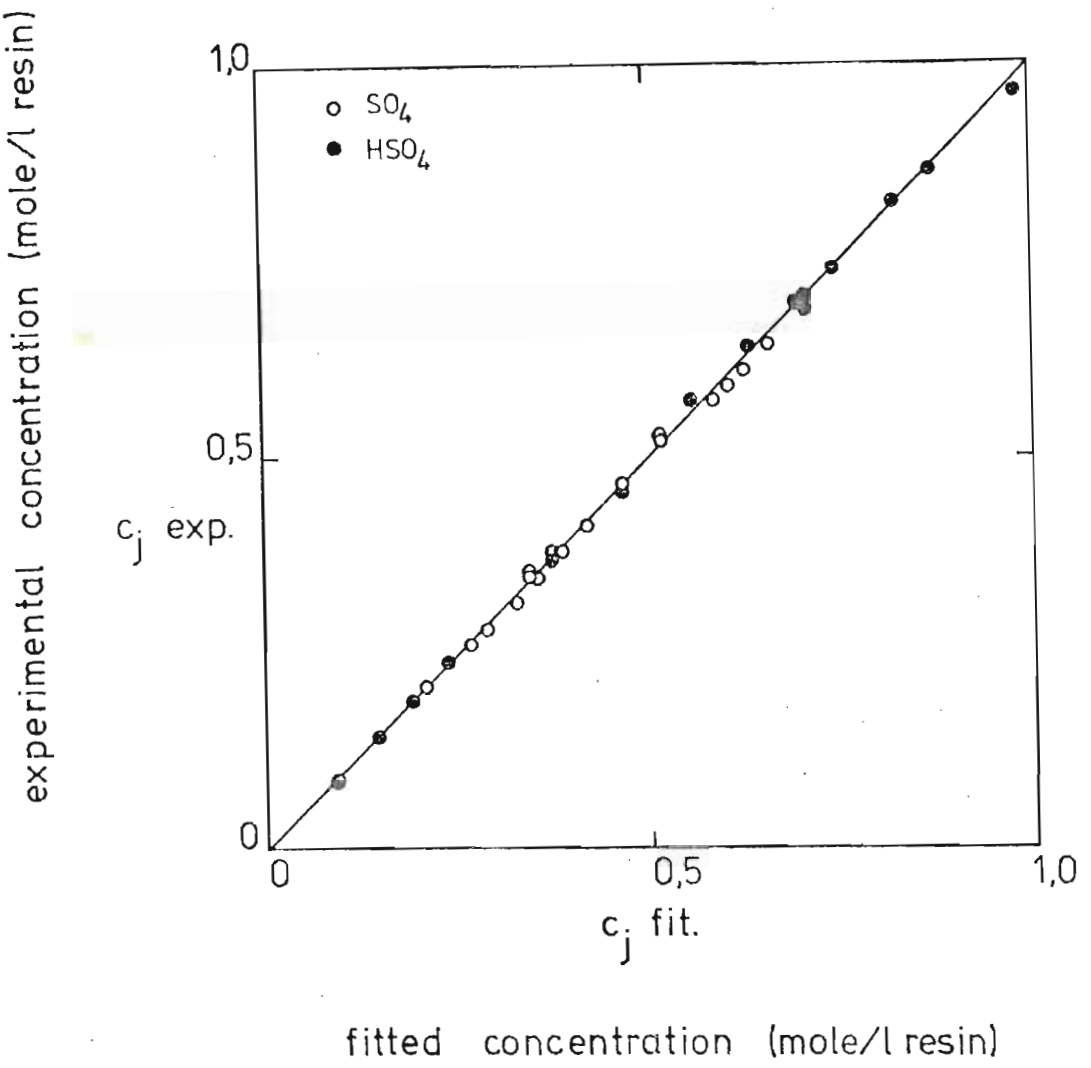


Figure 5.4 Comparison of fitted and experimental concentration on resin for binary system Amberlite 400, mixture of Na_2SO_4 and H_2SO_4 at 298°K. Capacity is 1,4 equiv./l resin. Wilson parameters and equilibrium constant used are reported in Figure 5.1. Tabulated data in Appendix Table F.8.

Expressions for the equilibrium constants are given by Equations (5.2) and (4.7) while those for the equilibrium quotients are given by Equations (5.3) and (4.8).

The equivalent balance equation for the resin phase is

$$2c_{SO_4} + c_{HSO_4} + c_{Cl} = \text{Capacity} \qquad (5.9)$$

A mass balance for sulphate is written as

$$c_{SO_4} + c_{HSO_4} = c_{\Sigma SO_4} \qquad (5.10)$$

There are two complex formation reactions in the solution phase for this system

$$H^+ + SO_4^{2-} \rightleftarrows HSO_4^- \qquad (5.11)$$

$$Na^+ + SO_4^{2-} \rightleftarrows NaSO_4^-$$

A. EXPERIMENTAL

The elution solution is 1 N $NaNO_3$. Unfortunately the high nitrate concentration makes the analysis for total sulphate in the eluate difficult. However the concentration of the sulphate form of the resin may be inferred from the equivalent balance, Equation (5.9)

$$c_{SO_4} = \frac{\text{Capacity} - c_{HSO_4} - c_{Cl}}{2.0}$$

The results obtained for this system are reported and discussed together with those of the following ternary system.

5.1.3 Characterisation of the ternary system SO_4^{2-} - HSO_4^- - NO_3^-

The ion exchange equilibria are determined for the system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$ and H_2SO_4 at 298^{o}K.

Equilibrium reactions for this system are

$$R_2SO_4 + 2HSO_4^- \rightleftarrows 2RHSO_4 + SO_4^{2-}$$

$$R_2SO_4 + 2NO_3^- \rightleftarrows 2RNO_3 + SO_4^{2-} \qquad (5.12)$$

Expressions for the equilibrium constants are given by Equations (5.2) and (4.2) and expressions for the equilibrium quotients are given by Equations (5.3) and (4.3).

The equivalent balance equation for the resin phase is

$$2c_{SO_4} + c_{HSO_4} + c_{NO_3} = \text{Capacity} \qquad (5.13)$$

A mass balance equation for sulphate is given by

$$c_{SO_4} + c_{HSO_4} = c_{\Sigma SO_4} \qquad (5.14)$$

Combining Equations (5.13) and (5.14)

$$c_{NO_3} = \text{Capacity} - 2c_{\Sigma SO_4} + c_{HSO_4} \qquad (5.15)$$

There are two complex formation reactions in the solution phase for this system

$$H^+ + SO_4^{2-} \rightleftarrows HSO_4^- \qquad (5.16)$$

$$Na^+ + SO_4^{2-} \rightleftarrows NaSO_4^-$$

A. EXPERIMENTAL

The elution solution is 1 N NaCl. The total sulphate concentration in the eluate is determined as outlined in Appendix E.2. The bisulphate concentration is determined from the analysis for acid as discussed in Appendix E.4.

The nitrate concentration has been inferred from the capacity, total sulphate and bisulphate according to Equation (5.15).

B. RESULTS AND DISCUSSION

The experimental equilibrium compositions of the resin and solution phases are summarised in Table 5.2 for the SO_4^{2-} - HSO_4^- - Cl^- systen in Table 5.3 for the SO_4^{2-} - HSO_4^- - NO_3^- ternary system.

For the SO_4^{2-} - HSO_4^- - Cl^- system the concentration of sulphate ions in the resin phase is inferred from the bisulphate and chloride ion concentration and the capacity of the resin, Equation (5.9).

For the SO_4^{2-} - HSO_4^- - NO_3^- system the sulphate ion concentration in the resin phase is inferred from the total sulphate and bisulphate ion concentrations, Equation (5.14). The nitrate concentration is inferred from the capacity, total sulphate and bisulphate ion concentrations, Equation (5.15).

Solution Phase				Resin Phase	
Mole/ℓ				Mole/ℓ Resin	
ΣSO_4	Cl	H	Na	HSO_4	Cl
0,2100	0,02	0,2400	0,2	0,780	0,1069
0,1963	0,04	0,2325	0,2	0,720	0,2006
0,1650	0,08	0,2100	0,2	0,600	0,3904
0,1375	0,12	0,1950	0,2	0,480	0,5861
0,1100	0,16	0,1800	0,2	0,388	0,7630
0,0850	0,18	0,1500	0,2	0,296	0,8736
0,1080	0,02	0,0360	0,2	0,276	0,1797
0,0969	0,04	0,0338	0,2	0,214	0,3321
0,0750	0,08	0,0300	0,2	0,154	0,6163
0,0520	0,12	0,0240	0,2	0,096	0,8567
0,0294	0,16	0,0188	0,2	0,050	1,0878
0,0175	0,18	0,0150	0,2	0,026	1,1851

Table 5.2 Equilibrium composition of solution and resin phases for system Amberlite 400, mixture of Na_2SO_4, NaCl and H_2SO_4 at 298°K. Capacity of resin is 1,4 equiv./l resin.

Solution Phase				Resin Phase		
Mole/ℓ				Mole /ℓ Resin		eq/ℓ Resin
ΣSO_4	NO_3	H	Na	ΣSO_4	HSO_4	Capacity
0,2100	0,02	0,2400	0,20	0,8576	0,6604	1,398
0,1966	0,04	0,2333	0,20	0,7085	0,5500	1,392
0,1658	0,08	0,2115	0,20	0,4918	0,3932	1,403
0,1394	0,12	0,1988	0,20	0,3401	0,2844	1,399
0,1104	0,16	0,1808	0,20	0,2373	0,2012	1,400
0,0869	0,18	0,1538	0,20	0,1816	0,1476	1,391
0,1086	0,02	0,0373	0,20	0,5448	0,2104	1,398
0,0970	0,04	0,0340	0,20	0,3992	0,1464	1,407
0,0753	0,08	0,0307	0,20	0,2202	0,0828	1,404
0,0526	0,12	0,0251	0,20	0,1174	0,0440	1,406
0,0303	0,16	0,0206	0,20	0,0514	0,0208	1,407
0,0188	0,18	0,0175	0,20	0,0248	0,0124	1,395

Table 5.3 Equilibrium composition of solution and resin phases for ternary system Amberlite 400, mixtures of Na_2SO_4, $NaNO_3$ and H_2SO_4 at 298°K.

The inferred ionic concentrations together with the basic equilibrium data enable the relevant equilibrium quotients to be determined.

The ternary systems under consideration may be decomposed and subsequently represented by pairs of binary systems. The parameters determined previously for these systems are applicable and as such significantly reduce the number of parameters required to characterise the ternary systems. In fact only the interaction coefficients for the HSO_4^-, Cl^- and HSO_4^-, NO_3^- pairs are outstanding.

Estimates of the interaction coefficients for the HSO_4^-, Cl^- pair are shown in Table 5.4. The agreement between the experimental and fitted equilibrium quotients obtained in the estimation is shown in Figures 5.5 and 5.6 for a root mean square error of ± 9% It is noted that the root mean square error increases with the increase in the number of components. The corresponding results for the HSO_4, NO_3 ion pair are shown in Table 5.5 and in Figures 5.8 and 5.9. The root mean square error for this estimation is ± 11%.

A comparison is made of the experimental and fitted resin compositions based on these parameters together with those of the binary systems determined previously. Results for the SO^{2-} - HSO_4^- - Cl^- system are shown in Figure 5.7 and for the SO_4^{2-} - HSO_4^- - NO_3^- system in Figure 5.10. It is noted that although a root mean square error of ± 11% was evident in the parameter estimation the errors in these results are generally less than ± 5%.

Wilson Parameters			RMS %
Λ_{ij}	HSO_4	Cl	
HSO_4	1,0	0,74146	± 9,3
Cl	1,2865	1,0	

Table 5.4 Estimates of the Wilson interaction coefficients for HSO_4^- and Cl^- pair in the ternary system Amberlite 400, Na_2SO_4, NaCl and H_2SO_4 at 298^oK

Wilson Parameters			RMS %
Λ_{ij}	HSO_4	NO_3	
HSO_4	1,0	2,6912	± 11,3
NO_3	0,27678	1,0	

Table 5.5 Estimates of the Wilson interaction coefficients for HSO_4^- and NO_3^- ion pair in the ternary system Amberlite 400, Na_2SO_4, $NaNO_3$ and H_2SO_4 at 298^oK

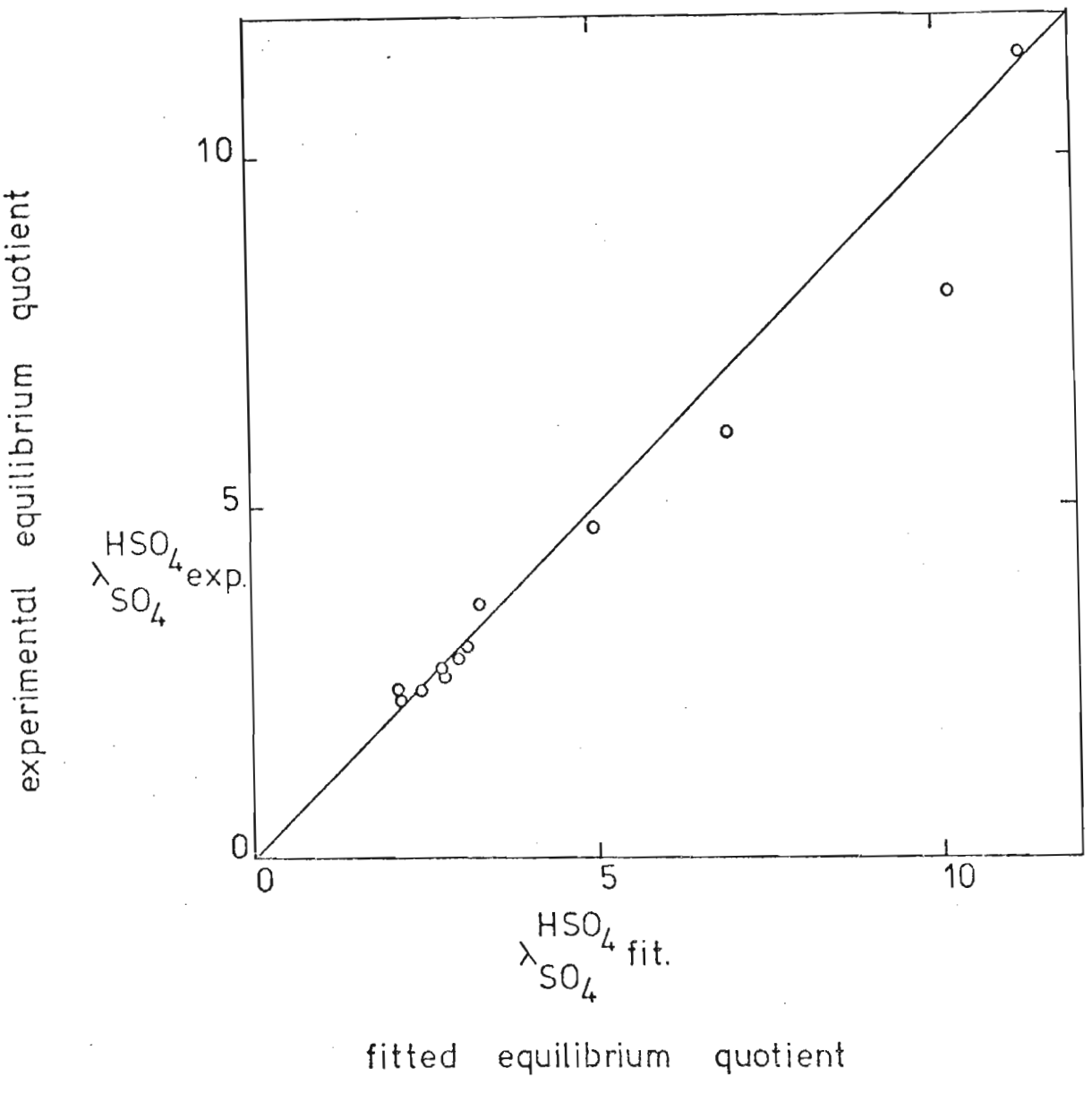


Figure 5.5 Comparison of fitted and experimental equilibrium quotients for system Amberlite 400, mixture of NaCl, Na_2SO_4 and H_2SO_4 at 298°K. Tabulated data in Appendix, Table F.9.

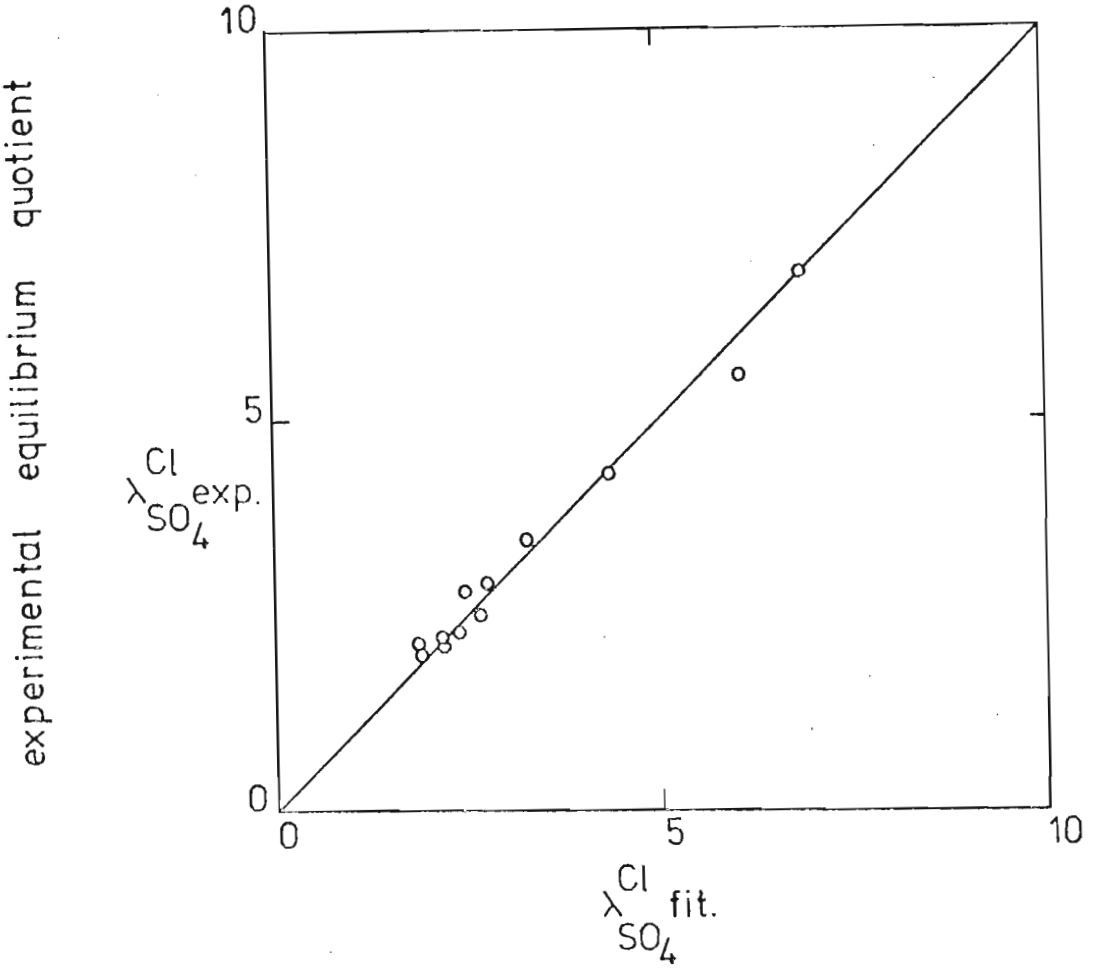


Figure 5.6 Comparison of fitted and experimental equilibrium quotients for system Amberlite 400, mixture of NaCl, Na_2SO_4 and H_2SO_4 at 298°K. Tabulated data in Appendix, Table F.9.

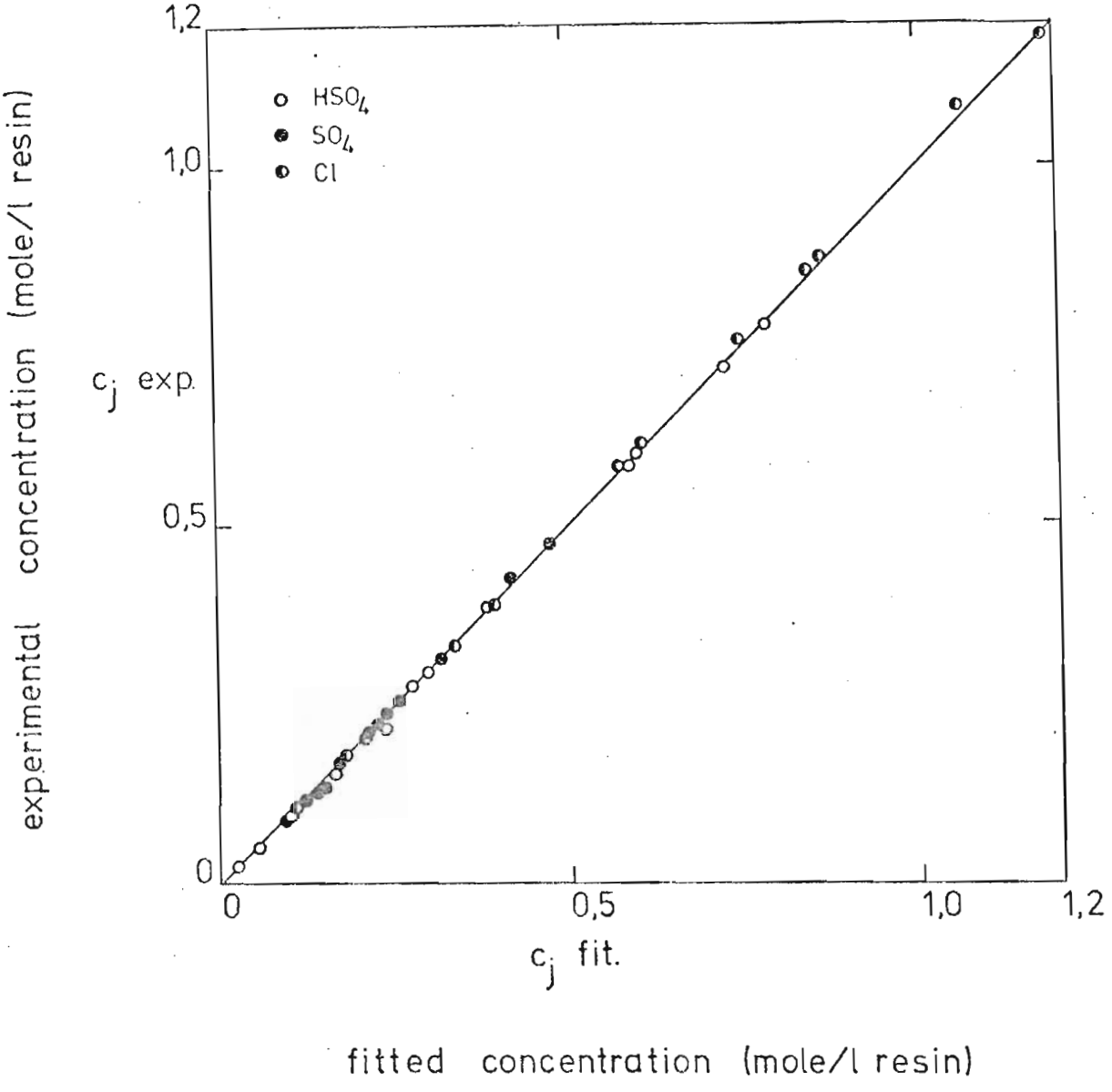


Figure 5.7 Comparison of fitted and experimental concentration on resin for system Amberlite 400, mixture of Na_2SO_4, NaCl and H_2SO_4 at 298°K. Tabulated data in Appendix, Table F.10.

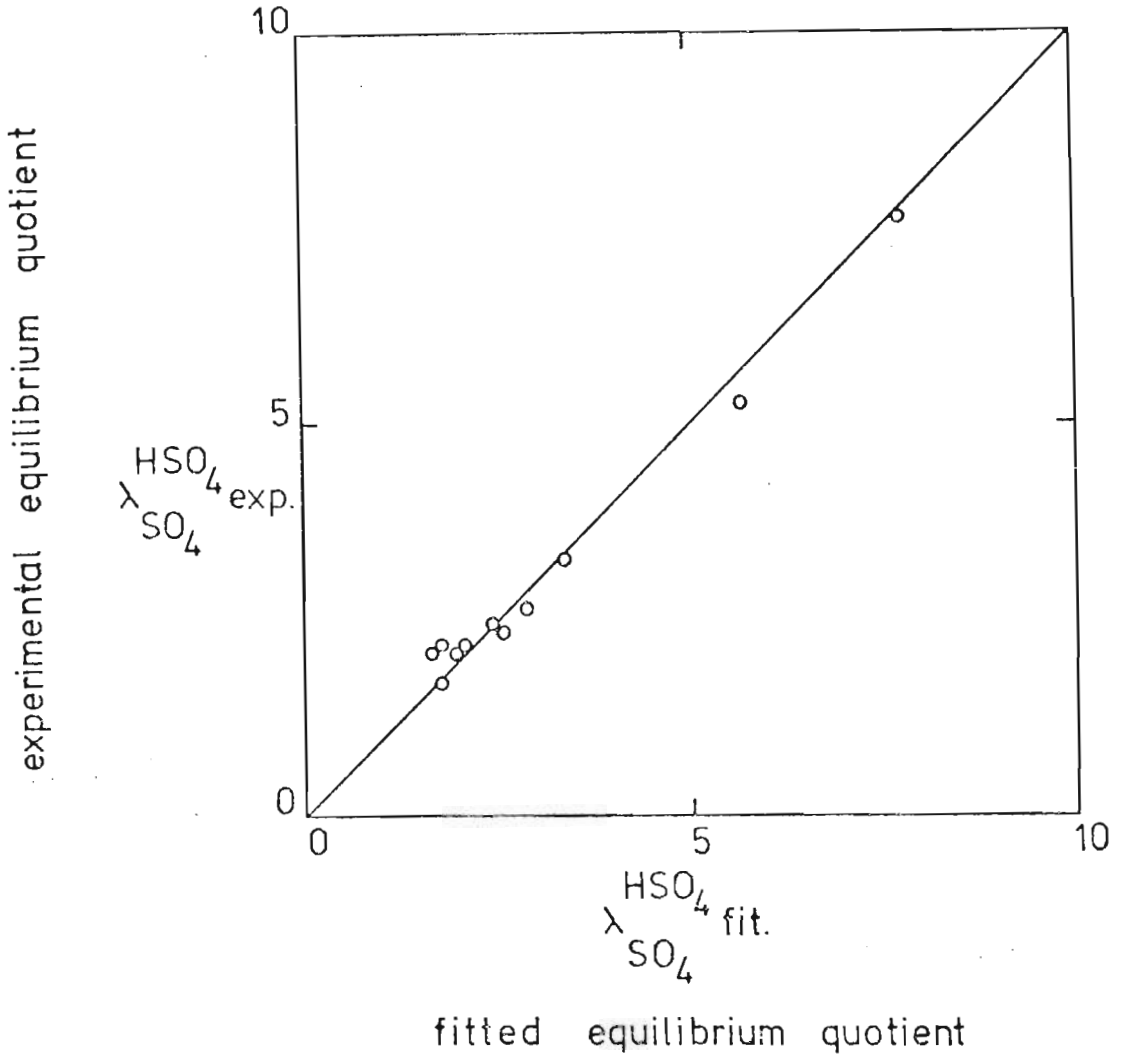


Figure 5.8 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of $NaNo_3$, Na_2SO_4 and H_2SO_4 at 298°K. Tabulated in data in Appendix, Table F.11.

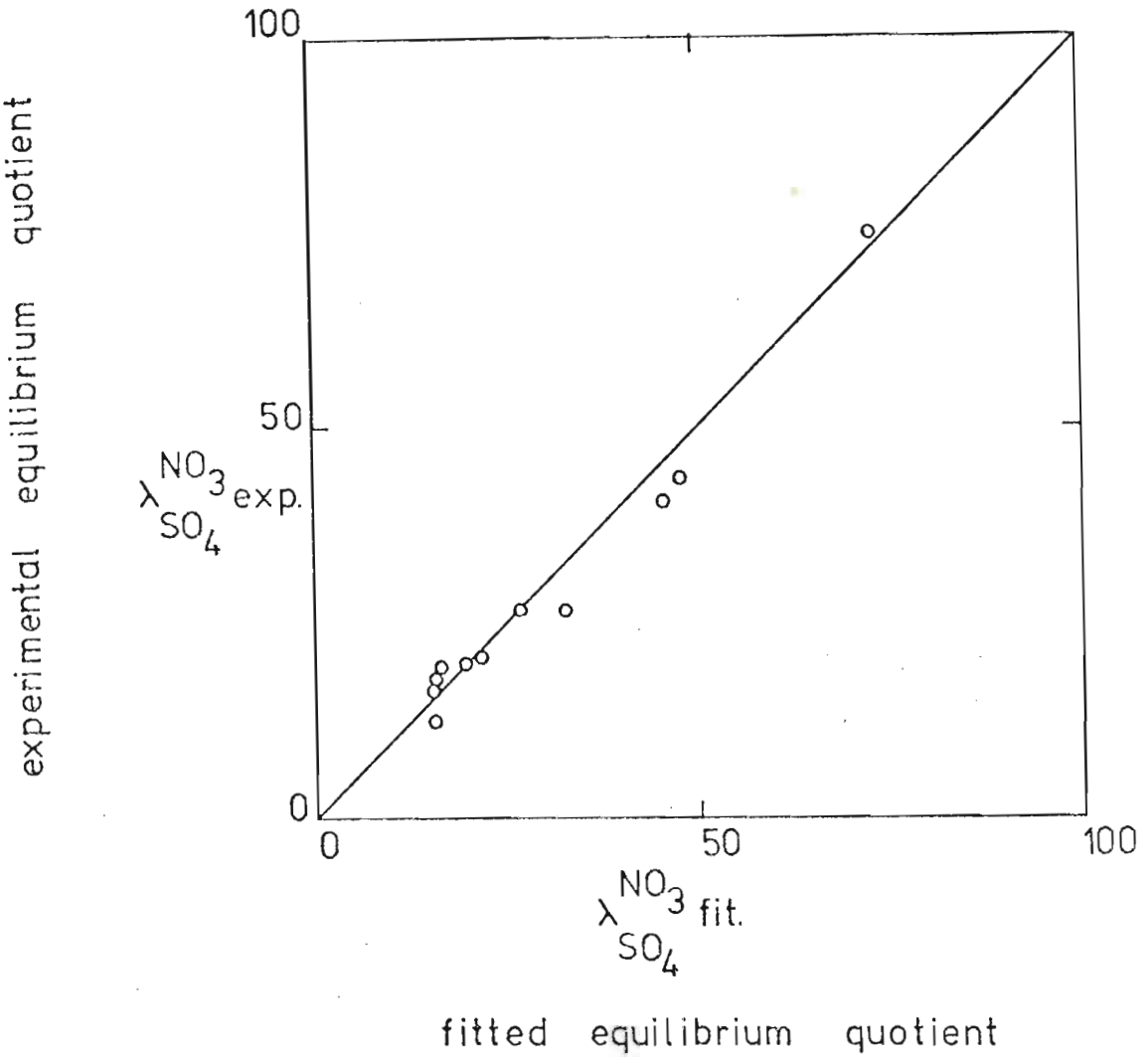


Figure 5.9 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of $NaNO_3$, Na_2SO_4 and H_2SO_4 at 298°K. Tabulated data in Appendix Table F.11.

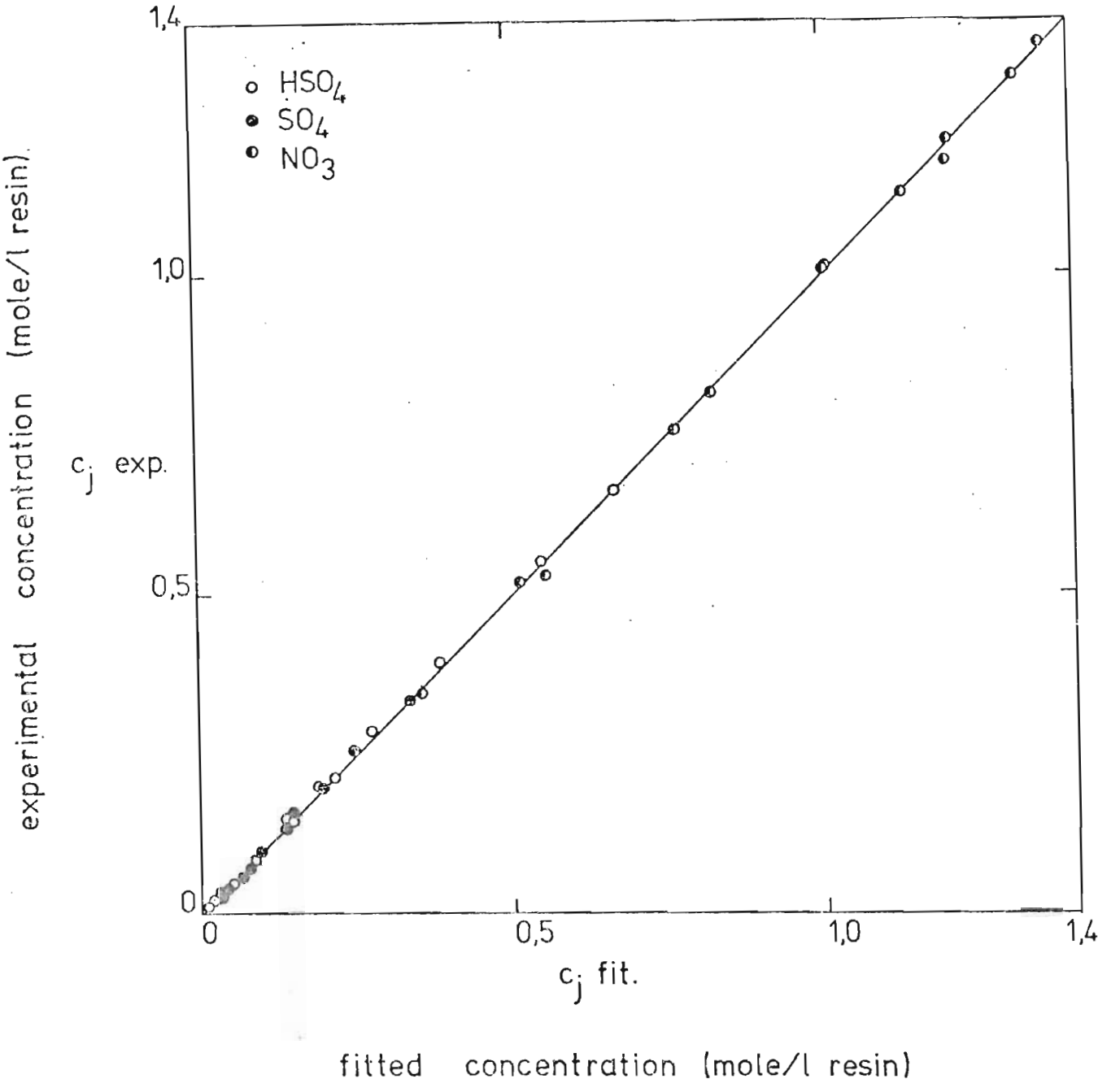


Figure 5.10 Comparison of fitted and experimental concentration on resin for system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$ and H_2SO_4 at 298°K. Tabulated data in Appendix Table F.12.

5.2 PREDICTION OF THE QUATERNARY SYSTEM SO_4^{2-} - HSO_4^- - NO_3^- - Cl^-

It is now possible to predict the equilibrium resin phase composition of this quaternary system from the characterisatics of the smallest subsystems measurable. These are the four binary systems SO_4^{2-} - NO_3^-, SO_4^{2-} - Cl^-, NO_3^- - Cl^- and SO_4^{2-} - HSO_4^- and the two ternary systems SO_4^{2-} - HSO_4^- - NO_3^- and SO_4^{2-} - HSO_4^- - Cl^-.

The interaction parameters and the equilibrium constants estimated for these systens only are combined through the Wilson equation to predict the equilibrium resin phase composition and activity coefficients for specified initial and solution conditions in Table 5.6.

The set of independent heterogeneous equilibrium reactions required to describe this system is

$$R_2SO_4 + 2HSO_4^- \rightleftarrows 2RHSO_4 + SO_4^{2-}$$

$$R_2SO_4 + 2Cl^- \rightleftarrows 2RCl + SO_4^{2-} \qquad (5.17)$$

$$R_2SO_4 + 2NO_3 \rightleftarrows 2RNO_3 + SO_4^{2-}$$

Two complex formation reactions occur in the solution phase

$$H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$$

$$Na^+ + SO_4^{2-} \rightleftarrows NaSO_4^- \qquad (5.18)$$

In the predictions a capacity of 1,4 equivalents per litre of free settled resin is assumed.

Specimen calculations of the activity of the solution species and the prediction of the resin phase composition are given in the Appendices J.2.1.A. and J.2.1.C respectively for the first experimental condition of Table 5.6.

5.2.1 Test experiments of the quarternary system SO_4^{2-} - HSO_4^- - NO_3^- - Cl^- for comparison with the predicted composition.

Ion exchange equilibria are determined for the system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$, NaCl and H_2SO_4 at 298°K.

The equivalent balance equation for the resin phase is expressed as

$$2c_{SO_4} + c_{HSO_4} + c_{Cl} + c_{NO_3} = \text{Capacity} \qquad (5.19)$$

A mass balance for sulphate species in the resin phase is given by

$$c_{SO_4} + c_{HSO_4} = c_{\Sigma SO_4} \qquad (5.20)$$

Combining Equations (5.19) and (5.20) determines the nitrate concentration in terms of measurable quantities

$$c_{NO_3} = \text{Capacity} - 2c_{\Sigma SO_4} - c_{Cl} + c_{HSO_4} \qquad (5.21)$$

A. EXPERIMENTAL

The elution solution for this system is 0,1 N $NaClO_4$. The chloride, acid and total sulphate concentration of the known volume of eluate is determined as described in the Appendix E. A capacity of 1,4 equivalents/litre resin is assumed. The nitrate concentration is inferred from Equation (5.21).

5.2.2 Results and Discussion

The predicted and experimental resin phase compositions are shown in Table 5.6 and Figure 5.11. The results are consistent over a moderately large range. Expressed on an equivalent fraction basis the range of experimental data is:

$$0,04 < y_{\Sigma SO_4} < 0,75$$

$$0,005 < y_{HSO_4} < 0,24$$

$$0,23 < y_{NO_3} < 0,71$$

$$0,14 < y_{Cl} < 0,57$$

The agreement between the experimental and predicted resin phase composition is within ± 10% as illustrated in Figure 5.11. The final four results in Table 5.6 represent two sets of duplicate experiments. The results show a high degree of reproducibility.

The quaternary system SO_4^{2-} - HSO_4^- - NO_3^- - Cl^- with one complex ion in the resin phase is successfully predicted from the characteristics of subsystems which represent the practical limit of the decomposition of the multiionic system.

Solution Phase (Mole/ℓ)					Resin Phase (Mole/ℓ Resin)							
					Experimental				Predicted			
ΣSO_4	Cl	NO_3	H	Na	ΣSO_4	HSO_4	NO_3^*	Cl	ΣSO_4	HSO_4	NO_3	Cl
0,15	0,08	0,02	0,120	0,280	0,5192	0,3484	0,3660	0,3440	0,5240	0,3453	0,3524	0,3449
0,15	0,08	0,02	0,030	0,370	0,3650	0,1198	0,4090	0,3808	0,3717	0,1233	0,3875	0,3924
0,10	0,08	0,12	0,080	0,320	0,1628	0,1182	0,9846	0,2080	0,1716	0,1122	0,9590	0,2100
0,10	0,08	0,12	0,020	0,380	0,1123	0,0376	0,9982	0,2148	0,1138	0,0347	0,9879	0,2191
0,09	0,20	0,02	0,072	0,328	0,2271	0,1462	0,3332	0,7588	0,2457	0,1438	0,3172	0,7352
0,09	0,20	0,02	0,018	0,382	0,1628	0,0482	0,3278	0,7948	0,1743	0,0456	0,3285	0,7685
0,04	0,20	0,12	0,032	0,368	0,0480	0,0296	0,8668	0,4668	0,0485	0,0247	0,8709	0,4567
0,04	0,20	0,12	0,008	0,392	0,0326	0,0080	0,8756	0,4672	0,0357	0,0071	0,8754	0,4603
0,12	0,12	0,04	0,096	0,304	0,3187	0,2144	0,5394	0,4376	0,3239	0,2076	0,5289	0,4309
0,12	0,12	0,04	0,024	0,376	0,2253	0,0696	0,5522	0,4668	0,2226	0,0680	0,5589	0,4639
0,12	0,12	0,04	0,096	0,304	0,3247	0,2140	0,5302	0,4344	0,3239	0,2076	0,5289	0,4309
0,12	0,12	0,04	0,024	0,376	0,2279	0,0700	0,5474	0,4668	0,2226	0,0680	0,5589	0,4639

Table 5.6 Comprison of experimental and predicted equilibrium composition of the quaternary system Amberlite 400, 0,4 N mixture of Na_2SO_4, $NaNO_3$, NaCl and H_2SO_4 at 298°K. Capacity assumed for predictions is 1,4 equiv./l resin. Results are presented graphically in Figure 5.11.

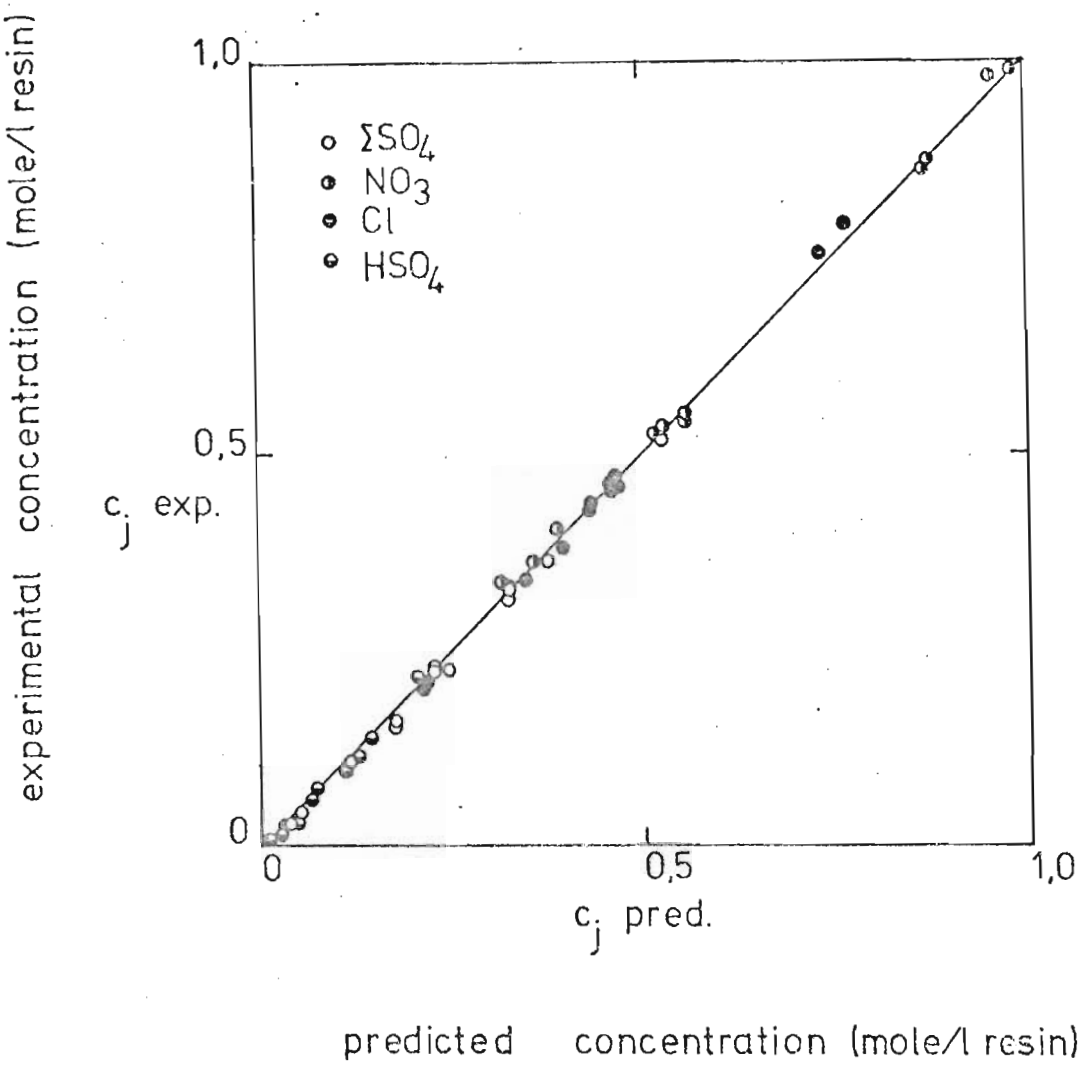


Figure 5.11 Comparison of predicted and experimental concentration for quaternary system Amberlite 400, mixture of NaCl, $NaNO_3$, Na_2SO_4 and H_2SO_4 at 298°K based on experimental data of binary and ternary systems. Tabulated results in Table 5.6.

CHAPTER SIX

INVESTIGATION OF URANIUM SYSTEMS RELATED TO THE TYPICAL SULPHURIC ACID LEACH LIQUOR

The relatively simple systems investigated in the previous chapters have produced very good results. The introduction of a cation such as the uranyl ion with its ability to complex with ligands in both phases is desirable to extend the application of the approach towards a real system such as that encountered in the extraction of uranium from leach liquors.

Unfortunately the introduction of multiple complexes in the resin phase reduces the effectiveness of the approach in that complexes imply subsystems of higher order than binary. Nevertheless the use of the characteristic of systems of lower order than that being considered significantly reduce the number of parameters to be estimated, this implies a smaller experimental effort.

This chapter includes the characterisation of the quaternary system Amberlite 400, mixture of uranyl sulphate, sodium sulphate and sulphuric acid. Two other quinary systems generated by the addition of the nitrate or chloride ions to the previous quaternary system are also investigated.

It is necessary to consider the quinary systems because they are the smallest subsystems which permit the estimation of the interaction parameters for ion pairs such as $UO_2(SO_4)_3^{4-}$, Cl^- and $UO_2(SO_4)_2^{2-}$, NO_3^-.

Once the quaternary and the two quinary systems are characterised it is possible to predict the six component system.

Before these systems may be characterised it is necessary to know what complexes are absorbed on the resin and to what extent. With this information reactions which represent the system may be proposed. The reactions selected do not necessarily imply reaction mechanisms since it is not possible to distinguish between reaction mechanisms from equilibrium data alone.

6.1 CHARACTERISATION EXPERIMENTS

6.1.1 Characterisation of the quaternary system SO_4^{2-} - HSO_4^- - $UO_2(SO_4)_3^{4-}$ - $UO_2(SO_4)_2^{2-}$

The ion exchange system, ion exchanger, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 has been investigated by many workers as indicated in Chapter 2. Equilibria have been obtained for this system using Amberilte 400 resin.

It is generally accepted (FINKELSTEIN and NEEDES, 1971, DEPTULA and MINC, 1967 and BANJERJEA and TRIPATHI, 1961) that the uranyl sulphate complexes in acidic sulphate solutions are given by the following reactions

$$UO_2^{2+} + SO_4^{2-} \rightleftarrows UO_2SO_4$$
$$UO_2^{2+} + 2SO_4^{2} \rightleftarrows UO_2(SO_4)_2^{2-} \qquad (6.1)$$

The other solution complexes formed are

$$H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$$
$$Na^+ + SO_4^{2-} \rightleftarrows NaSO_4^- \qquad (6.2)$$

This solution scheme is only valid for pH less than 3,0, above this pH uranyl hydroxy complexes are formed (STEIN, 1962). In practice due to the presence of ferric ions the acid concentration of leach liquors fed to the ion exchange columns is adjusted to pH 1,8 (AYERS and WESTWOOD, 1957).

Ferric ions are very important in industrial uranium extraction systems (JOHNSON and MILWARD, 1953). However the lack of information regarding the resin phase iron complexes and the difficulties encountered in ascertaining their stoichiometry has led to this ion being excluded from this study. A review of experimental techniques applicable to the identification of species in the resin phase is presented in Appendix H.

Accepting that the solution phase is adequately described by the reaction scheme, Equations (6.1) and (6.2), it is necessary to describe the resin phase before the ion exchange reactions are proposed. It is possible that more than one uranyl sulphate complex may be absorbed.

MAJCHRZAK (1971) has investigated the spectra of uranyl sulphate complexes absorbed on exchangers and has indicated that two complexes are present in the exchanger phase namely $UO_2(SO_4)_3^{4-}$ and $UO_2(SO_4)_2^{2-}$. These results are supported by mass balance considerations.

If ν is the average ligand number of the complex then an equivalent balance is

$$(2\nu - 2)\, C_{\Sigma U} + 2C_{SO_4} + C_{HSO_4} = \text{Capacity} \qquad (6.3)$$

The mass balance for the sulphate is

$$\nu C_{\Sigma U} + C_{SO_4} + C_{HSO_4} = C_{\Sigma SO_4} \qquad (6.4)$$

Combining Equations (6.3) and (6.4)

$$C_{HSO_4} = 2C_{\Sigma SO_4} - \text{Capacity} - 2C_{\Sigma U} \qquad (6.5)$$

MAJCHRZAK (1971) has assumed that for uranium concentrations less than 0,1 M the ratio k of sulphate to bisulphate in the resin phase is constant for a particular pH and total sulphate concentration in solution.

Introducing the ratio k, Equation (6.4) may be written including Equation (6.5)

$$\nu = \frac{C_{\Sigma SO_4} - (1 + k)\, C_{HSO_4}}{C_{\Sigma U}} \qquad (6.6)$$

or

$$\nu = \frac{C_{\Sigma SO_4} - (1 + k)\, (2C_{\Sigma SO_4} - \text{Capacity} - 2C_{\Sigma U})}{C_{\Sigma U}}$$

For known capacity, k, total sulphate and total uranium on the resin it is possible to infer the average ligand number.

Although STEIN (1962) and O'CONNOR (1954) have measured the bisulphate concentration in the resin phase the methods have not been successfully applied in this case and hence the inferred value of $C^{*}_{HSO_4}$ from Equation (6.5) is used in Equation (6.6).

Usually the predominant species are considered to be the exchanging species, however in this case the dominant species in the resin phase is not present in the solution phase. This suggests the possibility of absorption of neutral complexes and subsequent ligand association within the resin.

The following reactions are proposed based on the fact that $UO_2(SO_4)_3^{4-}$ and $UO_2(SO_4)_2^{2-}$ exist in the resin phase while UO_2SO_4 and $UO_2(SO_4)_2^{2-}$ are present in the solution phase.

$$2R_2SO_4 + UO_2SO_4 \rightleftarrows R_4UO_2(SO_4)_3$$

$$R_2SO_4 + UO_2(SO_4)_2^{2-} \rightleftarrows R_2UO_2(SO_4)_2 + SO_4^{2-} \qquad (6.7)$$

The first reaction representing an addition rather than an exchange process has been suggested by STREAT and GUPTA (1975) and POTTER (1975). In the solvent extraction of uranium and iron (III) from sulphuric acid solutions with alkylamines, DEPTULA and MINC (1967), SATO (1962) and CATTRALL and PEVERILL (1970) assume an interfacial extraction mechanism implied by the first reaction in Equation (6.7).

A further reaction occurs between sulphate and bisulphate ions

$$R_2SO_4 + 2HSO_4^- \rightleftarrows 2RHSO_4 + SO_4^{2-}$$

The equilibrium constants and quotients for this system are as follows

$$\lambda_{SO_4}^{HSO_4} = \frac{x_{HSO_4}^2 \; a'_{SO_4}}{x_{SO_4} \; a'^2_{HSO_4}} \quad , \quad K_{SO_4}^{HSO_4} = \frac{a_{HSO_4}^2 \; a'_{SO_4}}{a_{SO_4} \; a'^2_{HSO_4}}$$

$$\lambda_{SO_4}^{UO_2(SO_4)_3} = \frac{x_{UO_2(SO_4)_3}}{x_{SO_4}^2 \; a'_{UO_2SO_4}} \quad , \quad K_{SO_4}^{UO_2(SO_4)_3} = \frac{a_{UO_2(SO_4)_3}}{a_{SO_4}^2 \; a'_{UO_2SO_4}}$$

$$\lambda^{UO_2(SO_4)_2}_{SO_4} = \frac{x_{UO_2(SO_4)_2}\ a'_{SO_4}}{x_{SO_4}\ .\ a'_{UO_2(SO_4)_2}} \quad , \qquad K^{UO_2(SO_4)_2}_{SO_4} = \frac{a_{UO_2(SO_4)_2}\ a'_{SO_4}}{a_{SO_4}\ a'_{UO_2(SO_4)_2}}$$

A. EXPERIMENTAL

The elution solution is 1 N NaCl. The uranium concentration in the eluant is determined according to Appendix E.1. The total sulphate is determined according to Appendix E.2. Unfortunately the attempts to measure the bisulphate concentration were unsuccessful, however it may be inferred from Equation (6.5).

B. RESULTS AND DISCUSSION

The basic equilibrium data for the system, Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 is presented in Tables 6.1, 6.2 and 6.3. pH is the only activity measurement performed in the solution phase. As such it indicates with what accuracy the activity coefficients have been predicted.

The maximum difference between the experimental and predicted pH is 0,07 units with an average deviation of ± 0,03 units. A specimen calculation of the activity of solution phase species for this more complex system is shown in Appendix J.2.1.A.

Resin phase composition is expressed in moles per equivalent of exchanger for comparison with published data involving different resin samples. Comparison of the data with that in the literature is difficult because very few solution conditions correspond to those used in this work. Furthermore, the solution conditions are not always completely specified, in particular, the acid concentration

Solution Phase						Resin Phase				
(Mole / ℓ)				pH	pH Pred	(Mole / ℓ Resin)		(Equiv/ℓ Resin)	(Mole / Equiv Resin)	
ΣU	ΣSO_4	ΣH	Na			ΣU	ΣSO_4	Capacity	ΣU	ΣSO_4
0,000238	0,3641	0,0593	0,6689	2,00	2,03	0,1095	0,9707	1,416	0,0773	0,6855
0,000470	0,3641	0,0593	0,6689	2,00	2,03	0,1500	0,9783	1,420	0,1016	0,6889
0,000985	0,3641	0,0593	0,6689	2,00	2,03	0,1941	1,0118	1,432	0,1355	0,7066
0,001680	0,3641	0,0593	0,6689	2,00	2,03	0,2282	1,0041	1,380	0,1668	0,7276
0,003002	0,3641	0,0593	0,6689	2,00	2,03	0,2582	1,0709	1,436	0,1798	0,7458
0,003503	0,3641	0,0593	0,6689	2,00	2,03	0,2641	1,0709	1,416	0,1865	0,7563
0,000223	0,3619	0,1866	0,5373	1,50	1,45	0,0528	1,1296	1,435	0,0363	0,7872
0,000462	0,3619	0,1866	0,5373	1,50	1,45	0,0852	1,1279	1,422	0,0599	0,7932
0,000817	0,3619	0,1866	0,5373	1,50	1,45	0,1250	1,1525	1,428	0,0875	0,8071
0,001956	0,3619	0,1866	0,5373	1,50	1,44	0,1593	1,1094	1,386	0,1149	0,8004
0,002821	0,3619	0,1866	0,5373	1,50	1,44	0,1926	1,1198	1,402	0,1374	0,7987
0,003832	0,3619	0,1866	0,5373	1,50	1,44	0,2005	1,1142	1,398	0,1434	0,7970
0,000463	0,240	0,406	0,0731	0,85	0,79	0,0384	1,1805	1,413	0,0275	0,8355
0,00120	0,248	0,406	0,0876	0,85	0,80	0,0759	1,1617	1,416	0,0545	0,8204
0,00352	0,244	0,406	0,0750	0,85	0,79	0,1355	1,1720	1,418	0,0978	0,8265
0,000487	0,385	0,406	0,3630	0,95	0,95	0,0326	1,1634	1,417	0,0235	0,8210
0,00122	0,388	0,406	0,3680	0,95	0,97	0,0684	1,1685	1,415	0,0496	0,8258
0,00358	0,392	0,406	0,3708	0,95	0,97	0,1263	1,1685	1,410	0,0920	0,8287
0,000451	0,578	0,3701	0,7850	1,17	1,18	0,0306	1,1600	1,412	0,0221	0,8215
0,001279	0,583	0,3701	0,7933	1,15	1,18	0,0668	1,1823	1,415	0,0480	0,8356
0,003603	0,587	0,3701	0,7967	1,15	1,18	0,1258	1,1874	1,415	0,0905	0,8392

Table 6.1 Equilibrium composition of both phases for system Amberlite 400, mixture of Na_2SO_4 and UO_2SO_4 at 298°K.
Comparison of experimental and predicted pH of solution phase.

Solution Phase						Resin Phase				
(Mole /ℓ)				pH	pH Pred	(Mole /ℓ Resin)		(Equiv/ℓ Resin)	(Mole / Equiv Resin)	
ΣU	ΣSO_4	ΣH	Na			ΣU	ΣSO_4	Capacity	ΣU	ΣSO_4
0,000484	0,242	0,1855	0,2975	1,30	1,33	0,0910	1,0743	1,409	0,0659	0,7625
0,001173	0,245	0,1855	0,3022	1,30	1,33	0,1346	1,0914	1,414	0,0974	0,7719
0,003765	0,255	0,1855	0,3170	1,30	1,34	0,2066	1,1052	1,410	0,1497	0,7838
0,000478	0,383	0,1858	0,5792	1,40	1,47	0,0767	1,0743	1,416	0,0552	0,7587
0,001147	0,391	0,1858	0,5939	1,40	1,47	0,1216	1,0692	1,406	0,0875	0,7605
0,003617	0,395	0,1858	0,5970	1,40	1,47	0,1912	1,1086	1,401	0,1365	0,7913
0,000450	0,600	0,1868	1,0125	1,58	1,58	0,0696	1,0709	1,407	0,0495	0,7611
0,001247	0,601	0,1868	1,0125	1,60	1,58	0,1172	1,0760	1,413	0,0829	0,7615
0,003687	0,603	0,1868	1,0125	1,60	1,58	0,1839	1,0880	1,407	0,1307	0,7733
0,000543	0,237	0,0577	0,4152	1,95	1,95	0,1635	0,9903	1,417	0,1174	0,6989
0,001193	0,248	0,0577	0,4359	1,95	1,96	0,2030	1,0212	1,412	0,1457	0,7232
0,003813	0,252	0,0577	0,4387	1,95	1,96	0,2649	1,0452	1,407	0,1928	0,7429
0,000485	0,386	0,0591	0,7118	2,00	2,05	0,1381	0,9715	1,410	0,1019	0,6890
0,001223	0,391	0,0591	0,7205	2,00	2,05	0,1946	1,0041	1,415	0,1401	0,7096
0,003647	0,405	0,0591	0,7436	2,00	2,05	0,2453	1,0469	1,412	0,1766	0,7414
0,000471	0,581	0,0584	1,1026	2,05	2,13	0,1306	0,9681	1,417	0,0938	0,6832
0,001200	0,586	0,0584	1,1112	2,05	2,13	0,1707	1,0161	1,409	0,1237	0,7212
0,003650	0,588	0,0584	1,1103	2,05	2,13	0,2356	1,0606	1,404	0,1707	0,7554

Table 6.2 Equilibrium composition of both phases for system Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Comparison of experimental and predicted pH of solution phase.

Solution Phase						Resin Phase				
(Mole / ℓ)				pH	pH Pred	(Mole /ℓ Resin)		(Equiv /ℓ Resin)	(Mole / Equiv Resin)	
ΣU	ΣSO_4	ΣH	Na			ΣU	ΣSO_4	Capacity	ΣU	ΣSO_4
0,01	0,3971	0,3692	0,405	1,05	1,03	0,2125	1,1805	1,416	0,1501	0,8337
0,03	0,3971	0,3692	0,365	1,00	1,00	0,3035	1,1977	1,403	0,2163	0,8537
0,10	0,3971	0,3692	0,225	0,90	0,91	0,4307	1,2885	1,398	0,3081	0,9217
0,01	0,258	0,2960	0,20	1,08	1,02	0,2417	1,1189	1,405	0,1720	0,7964
0,03	0,278	0,2960	0,20	1,05	1,01	0,3311	1,1206	1,412	0,2345	0,7936
0,10	0,348	0,2960	0,20	1,00	0,99	0,4578	1,2465	1,404	0,3261	0,8878
0,01	0,3978	0,1831	0,5924	1,50	1,47	0,2568	1,0657	1,404	0,1829	0,7591
0,03	0,3978	0,1831	0,5524	1,45	1,44	0,3417	1,0520	1,412	0,2420	0,7450
0,10	0,3978	0,1831	0,4124	1,30	1,34	0,4693	1,1634	1,401	0,3350	0,8304
0,01	0,1656	0,1112	0,20	1,50	1,49	0,3119	1,0657	1,416	0,2203	0,7526
0,03	0,1856	0,1112	0,20	1,50	1,48	0,3985	1,0974	1,400	0,2846	0,7839
0,10	0,2556	0,1112	0,20	1,40	1,44	0,5379	1,2268	1,400	0,3842	0,8763
0,01	0,3996	0,0592	0,72	2,10	2,04	0,3046	1,0298	1,416	0,2151	0,7273
0,03	0,3996	0,0592	0,68	2,05	2,02	0,3869	1,1000	1,398	0,2768	0,7868
0,10	0,3966	0,0592	0,54	1,90	1,92	0,5124	1,1874	1,393	0,3678	0,8524

Table 6.3 Equilibrium composition of both phases for system Amberlite 400, mixture of Na_2So_4, H_2SO_4 and UO_2SO_4 at 298°K. Comparison of experimental and predicted pH of solution phase.

is not indicated instead the pH is reported. Consequently a calculation of the expected resin composition is not possible. The few results that may be compared with the literature are reasonable, see Appendix G for a compilation of literature data for this system.

In the approach to calculate the average ligand number of the uranyl sulphate complexes the molar ratio k between the sulphate and bisulphate ion concentration in the resin phase is correlated with the activity of the bisulphate ion in the solution phase.

The data from the binary ststem SO_4^{2-} - HSO_4^- in Chapter 5 has been used. The results are shown in Table 6.4 and Figure 6.1. The coefficients of the correlation equation have been estimated using a multilinear regression routine. The equation obtained is

$$\log_{10} k = - 1,4383 - 1,178 \log_{10} a'_{HSO_4} - 0,09122 (\log_{10} a'_{HSO_4})^2$$

Standard error of estimate is 0,02338.

With the value of k and the concentration of the bisulphate ion in the resin phase calculated from the charge balance, Equation (6.5) it is possible to determine the average ligand number of the uranyl sulphate complexes in the resin phase. The results are shown in Table 6.4 and Figure 6.2 where the calculated average ligand number has been plotted against the total uranium concentration in the solution. It is seen that the precision decreases rapidly at total uranium concentrations in the solution below 0,001 M.

For comparison the data of MAJCHRAZAK (1971), determined similarly and qualified with spectral data, has been included in Figure 6.2

a'_{HSO_4} (Mole /ℓ)	k	HSO_4^* (Mole /Lres)	ν Average Ligand Number
2999 10^{-1}	1,3938	0,3064	2,167
2999 10^{-1}	1,3938	0,2366	2,746
2998 10^{-1}	1,3944	0,2034	2,704
2996 10^{-1}	1,3953	0,1718	2,597
2992 10^{-1}	1,3968	0,1994	2,297
2991 10^{-1}	1,3974	0,1976	2,261
9038 10^{-1}	0,4921	0,7186	1,087
9035 10^{-1}	0,4922	0,6634	1,619
9030 10^{-1}	0,4925	0,6270	1,734
9016 10^{-1}	0,4933	0,5142	2,144
9005 10^{-1}	0,4939	0,4524	2,305
8992 10^{-1}	0,4946	0,4294	2,356
1384	0,3208	0,8712	0,777
1408	0,3152	0,7556	2,216
1384	0,3207	0,6550	2 265
1736	0,2539	0,8446	3,201
.739	0,2536	0,7852	2,693
.738	0,2536	0,6744	2,558
.762	0,2500	0,8468	3,317
.763	0,2499	0,8160	2,431
762	0,2501	0,7082	2,401

a'_{HSO_4} (Mole /ℓ)	k	HSO_4^* (Mole /Lres)	ν Average Ligand Number
0,8438 10^{-1}	0,5265	0,5576	2,452
0,8450 10^{-1}	0,5258	0,4996	2,445
0,8483 10^{-1}	0,5238	0,3872	2,494
0,9050 10^{-1}	0,4914	0,5792	2,744
0,9061 10^{-1}	0,4908	0,4892	2,795
0,9050 10^{-1}	0,4914	0,4338	2,414
0,9310 10^{-1}	0,4778	0,5956	2,740
0,9308 10^{-1}	0,4779	0,5046	2,818
0,9299 10^{-1}	0,4784	0,4012	2,691
0,2867 10^{-1}	1,4512	0,2366	2,510
0,2874 10^{-1}	1,4484	0,2244	2,324
0,2869 10^{-1}	1,4506	0,1536	2,525
0,2993 10^{-1}	1,3963	0,2568	2,578
0,2993 10^{-1}	1,3965	0,2040	2,648
0,2991 10^{-1}	1,3974	0,1912	2,399
0,2964 10^{-1}	1,4085	0,2580	2,655
0,2964 10^{-1}	1,4088	0,2818	1,976
0,2961 10^{-1}	1,4098	0,2460	1,986

a'_{HSO_4} (Mole /ℓ)	k	HSO_4^* (Mole /Lres)	ν Average Ligand Number
0,1616	0,2736	0,5200	2,439
0,1563	0,2827	0,3854	2,318
0,1374	0,3230	0,3176	2,016
0,1188	0,3747	0,3494	2,642
0,1166	0,3815	0,1670	2,688
0,1104	0,4031	0,1734	2,191
0,8886 10^{-1}	0,5004	0,2138	2,901
0,8726 10^{-1}	0,5094	0,0086	3,041
0,8009 10^{-1}	0,5541	-0,0128	-
0,4922 10^{-1}	0,8837	0,0916	3,362
0,4799 10^{-1}	0,9050	-0,0022	-
0,4441 10^{-1}	0,9729	-0,0222	-
0,2985 10^{-1}	1,3997	0,0344	3,1098
0,2951 10^{-1}	1,4144	0,0282	2,667
0,2789 10^{-1}	1,4875	-0,0430	-

Table 6.4 Calculation of the average ligand number, ν of the uranyl sulphate complex in the resin phase based on Equation (6.6) for the system Amberlite 400, mixture of Na_2SO_4 and UO_2SO_4 at 298°K. This data is presented graphically in Figures 6.1 and 6.2.

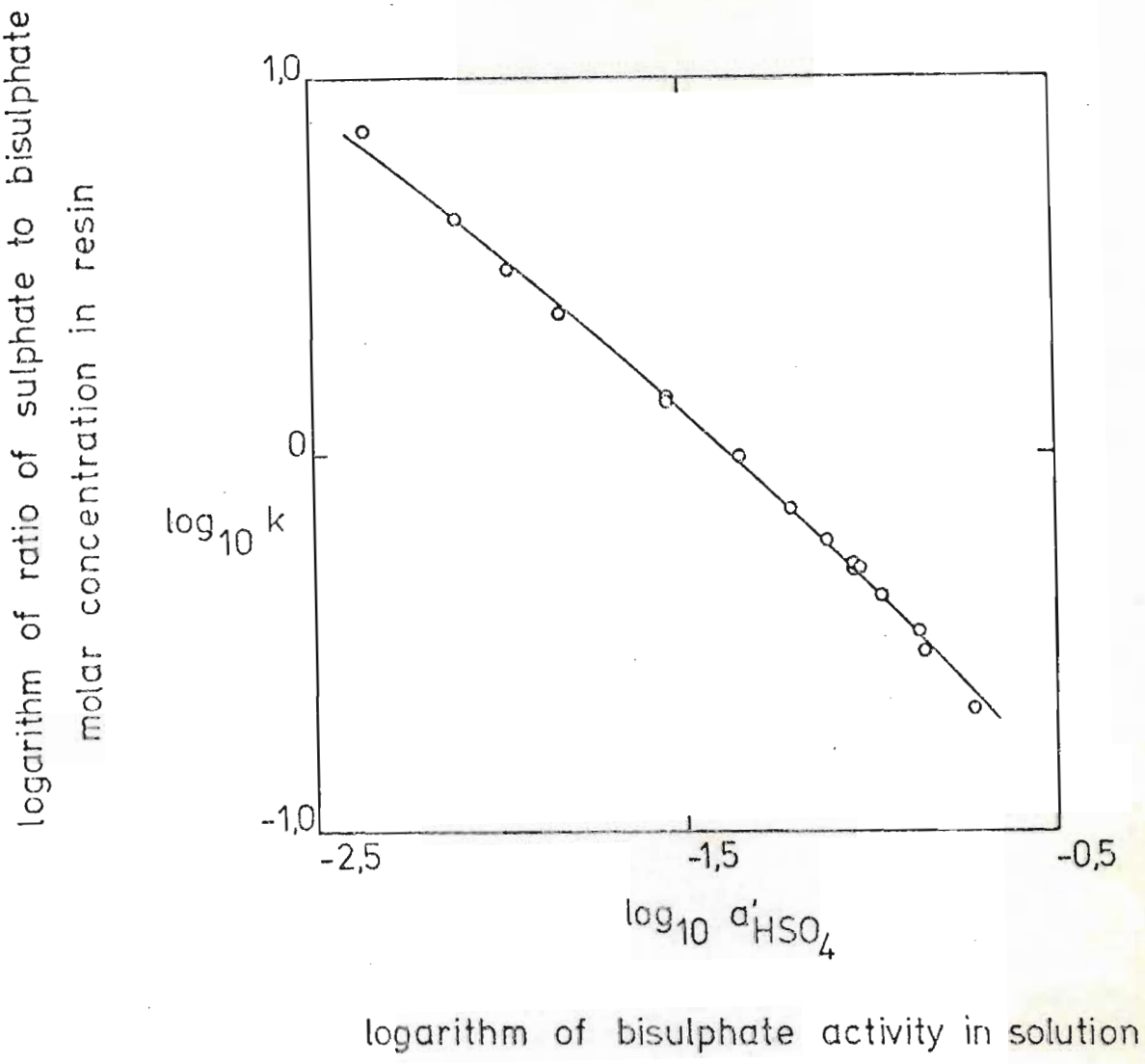


Table 6.1 Correlation of the molar ratio of sulphate to bisulphate ion in resin with activity of bisulphate ion in solution phase for binary systems Amberlite 400, mixture of Na_2SO_4 and H_2SO_4 at 298°K. Tabulated data is presented in Table 6.4.

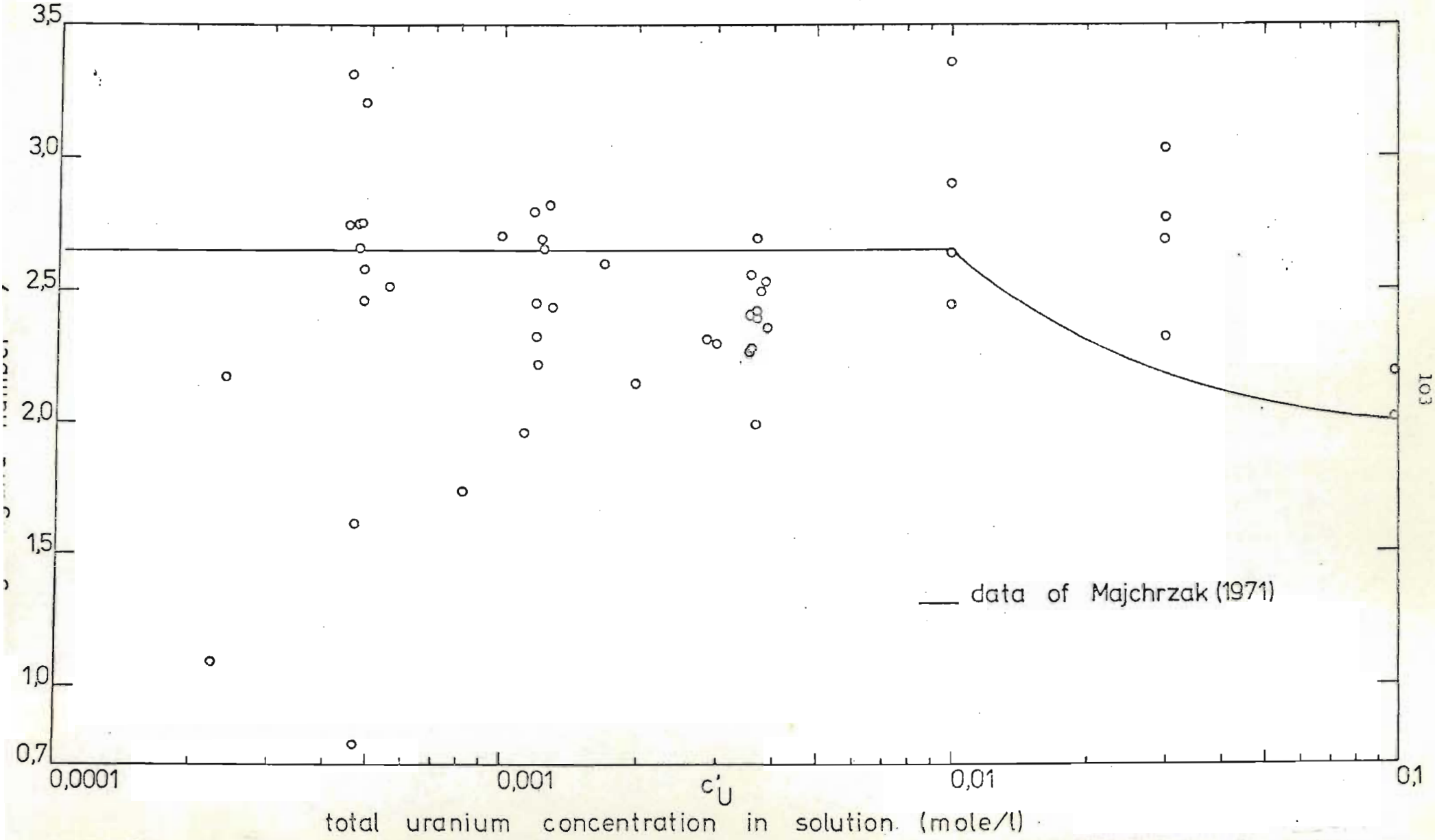


Figure 6.2 Average ligand number of the uranyl sulphate complex calculated from the experimental data for system Amberlite 400, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K compared with data of MAJCHRZAK (1971). Tabulated data in Table 6.4.

as a solid line. According to MAJCHRAZAK (1971) the effect of the solution conditions on the average ligand number is very small for solutions with total sulphate concentrations less than 1 M and pH less than 2,5 over the entire range of uranium concentrations considered. The large deviations of these results indicate that the analyses are not sufficiently accurate for this treatment.

An alternative approach adopted assumes the data of MAJCHRAZAK (1971) as valid and estimates the bisulphate ion concentration on the resin in the following way.

A plot of binary data for the system SO_4^{2-} - HSO_4^- in the form $a'_{SO_4}/(a'_{HSO_4})^2$ versus y_{HSO_4} is used to obtain a correlation shown in Figure 6.3. The coefficients are estimated using a multilinear regression routine. The resultant equation is

$$y_{HSO_4} = 0,64657 - 0,2668 \log_{10} \frac{a'_{SO_4}}{(a'_{HSO_4})^2} + 0,01409 \left(\log_{10} \frac{a'_{SO_4}}{(a'_{HSO_4})^2} \right)^3$$

$$- 0,001799 \left(\log_{10} \frac{a'_{SO_4}}{(a'_{HSO_4})^2} \right)^4$$

The standard error of estimate is 0,0077.

For the complex system being characterised $a'_{SO_4}/(a'_{HSO_4})^2$ is known, this implies a certain equivalent fraction y_{HSO_4}. If it is assumed that the presence of uranium on the resin effectively reduces the capacity for SO_4^{2-} and HSO_4^-, then the concentration of HSO_4^- is easily obtained.

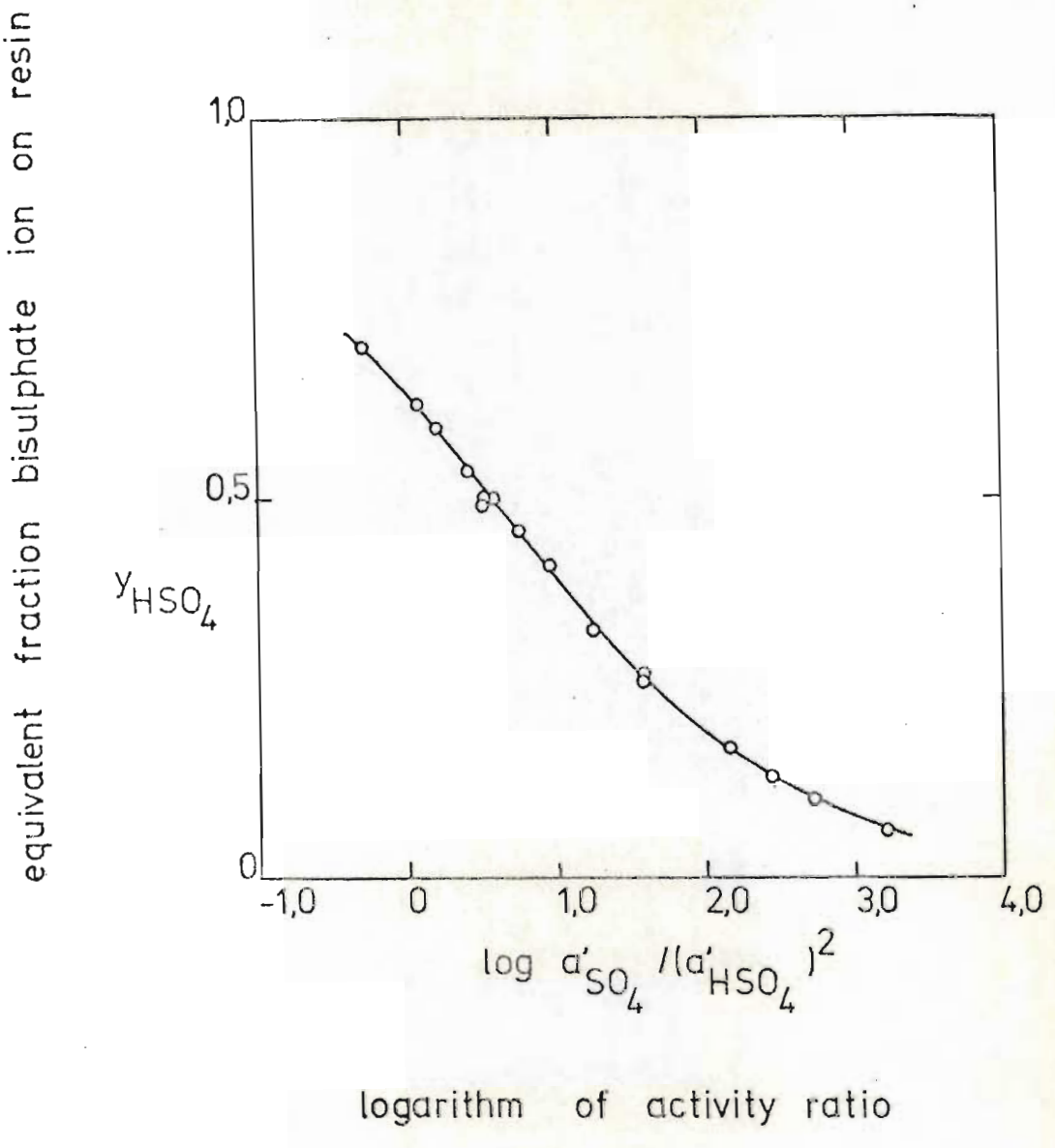


Figure 6.3 Correlation of bisulphate ion equivalent fraction on resin with logarithms of activity ratio of sulphate and bisulphate ions in solution phase for binary system Amberlite 400, mixture Na_2SO_4 and H_2SO_4 at 298°K.

With the value of the average ligand number specified and the bisulphate ion concentration calculated in this manner it is possible to determine the ion concentration of the remaining species without using the experimental value for the total sulphate on the resin. This extra measurement allows a check to be made of this assumption as shown in the Appendix Table F.16. The species distribution in mole fractions is determined and thereafter the equilibirum quotients. A specimen calculation of the equilibrium quotient for the first experiment in Table 6.1 is presented in Appendix J.4.

Equilibrium constants for the two resin reactions involving the uranium complexes are two of the parameters to be estimated from the data. Using the Wilson interaction coefficients of all relevant previous subsystems the total number of undetermined parameters is reduced to twelve.

The results of the parameter estimation are shown in Table 6.5. It is noted that the root mean square error for this four component system is ± 17,6% which is significantly higher than that obtained for the subsystems investigated. It is also noted that two of the interaction coefficients are significantly smaller than those previously estimated, while two are slightly higher. Nevertheless if the hypothetical binary systems are generated from these four components it may be seen that those systems with the very small interaction coefficients retain the feature that the one coefficient is greater than unity while the other is smaller than unity. The remaining binary systems have coefficients in the range, 0,6 - 5,2 which are quite acceptable.

Ion Exchange Reaction	Parameters Estimated						RMS %
	Equilibrium Constant	Wilson Parameters					
		Λ_{ij}	SO_4	HSO_4	$UO_2(SO_4)_3$	$UO_2(SO_4)_2$	
$2R_2SO_4 + UO_2SO_4 \rightleftarrows R_4UO_2(SO_4)_3$	$K_{SO_4}^{UO_2(SO_4)_3} = 7381,8$	SO_4	1,0	-	4,8276	5,2322	± 17,6
$R_2SO_4 + UO_2(SO_4)_2 \rightleftarrows R_2UO_2(SO_4) + SO_4$	$K_{SO_4}^{UO_2(SO_4)_2} = 41,408$	HSO_4	-	1,0	2,8237	0,81317	
		$UO_2(SO_4)_3$	0,0026155	0,62344	1,0	0,036596	
		$UO_2(SO_4)_2$	1,7304	0,85263	1,7655	1,0	

Table 6.5 Estimates of the Equilibrium Constants and Wilson parameters for the system Amberlite 400, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Root mean square error of the experimental and fitted equilibrium quotients.

Comparison of the experimental and fitted equilibrium quotient is made in Figures 6.4, 6.5 and 6.6. Discrepancies are seen to be large in some cases due to small errors in the resin phase analysis which are compounded by the calculation of the equilibrium quotients.

The deviations between the experimental and fitted resin compositions are very much less than those of the equilibrium quotients as seen from Figure 6.7. A sample calculation of the fitted resin phase composition of this more complex system is shown in Appendix J.2.1.C.

It is noted that although the experimental total sulphate values were not used in the calculations the agreement between the experimental and fitted total sulphate on the resin is generally better than ± 5%, refer to Appendix Table F.16. This suggests that the assumptions made in calculating the bisulphate ion concentration are reasonable.

6.1.2 Characterisation of the quinary system SO_4^{2-} - HSO_4^- - $UO_2(SO_4)_3^{4-}$ - $UO_2(SO_4)_2^{2-}$ - NO_3^-

The ion exchange equilibria for the system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$, H_2SO_4 and UO_2SO_4 are determined at 298°K.

Although the nitrate ligand forms complexes with the uranyl cation in the aqueous phase the stability constants measured by BANERJEA and TRIPATHI (1961) are extremely small. YOSHIMURA *et al* (1962) have assumed that no uranyl nitrate complexes exist in the solution in their studies on metal complex species by ion exchange.

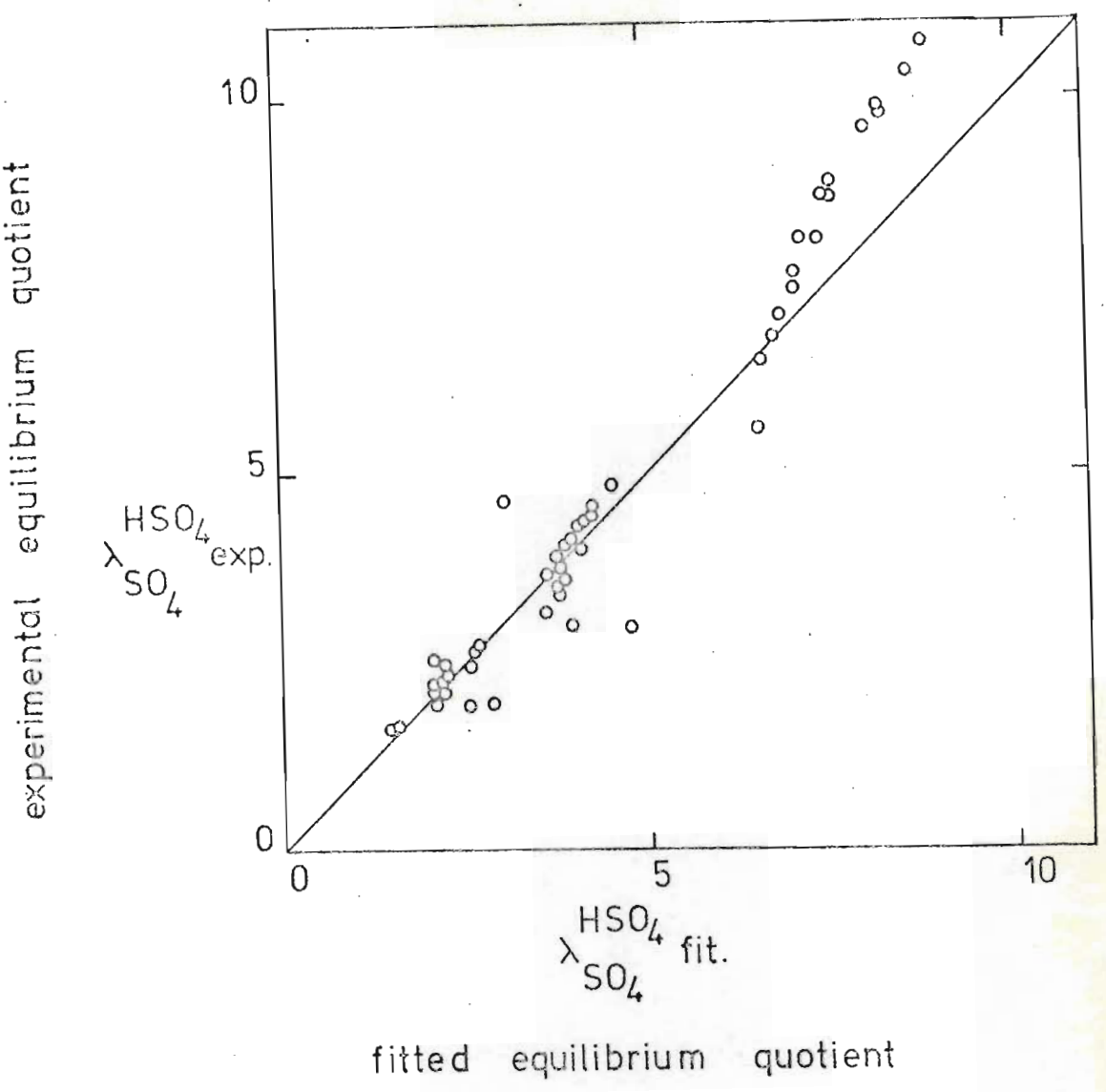


Figure 6.4 Comparison of fitted and experimental equilibrium quotient for systems. Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298° K. Tabulated data in appendix Tables F.13, F.14 and F.15.

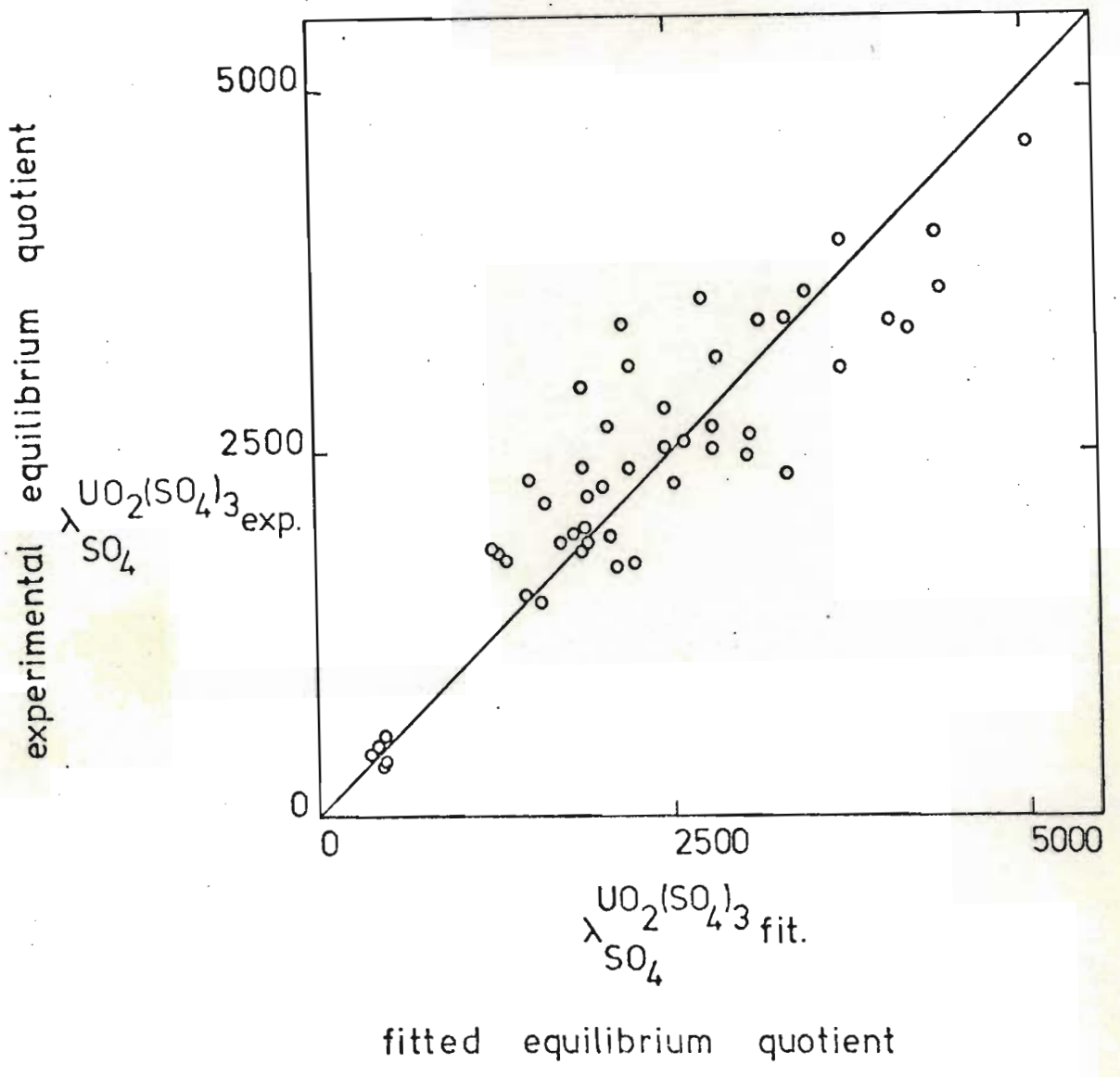


Figure 6.5 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Tabulated data in Appendix Tables F.13, F.14 and F.15.

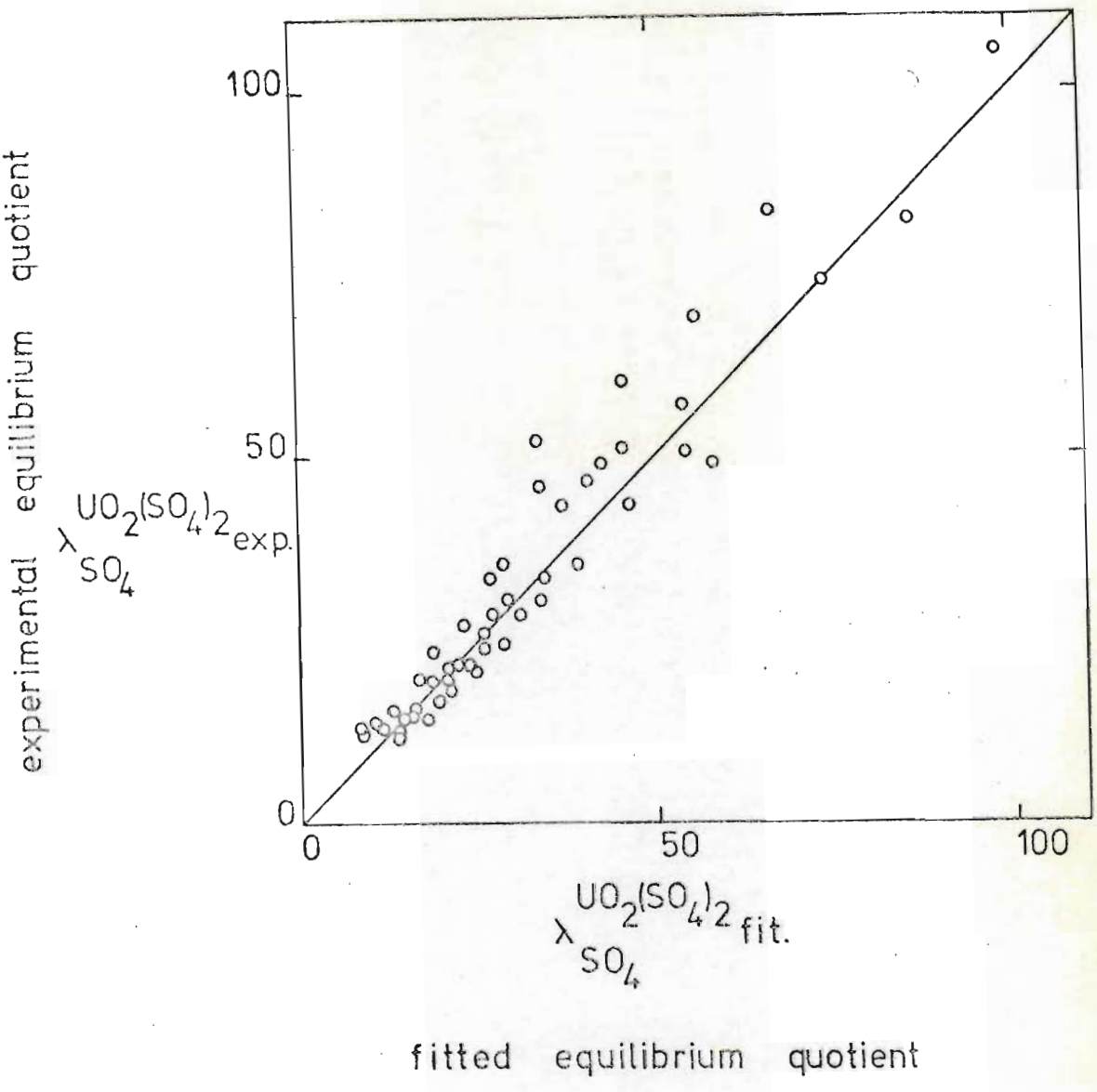


Figure 6.6 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Tabulated data in Appendix Tables F.13, F.14 and F.15.

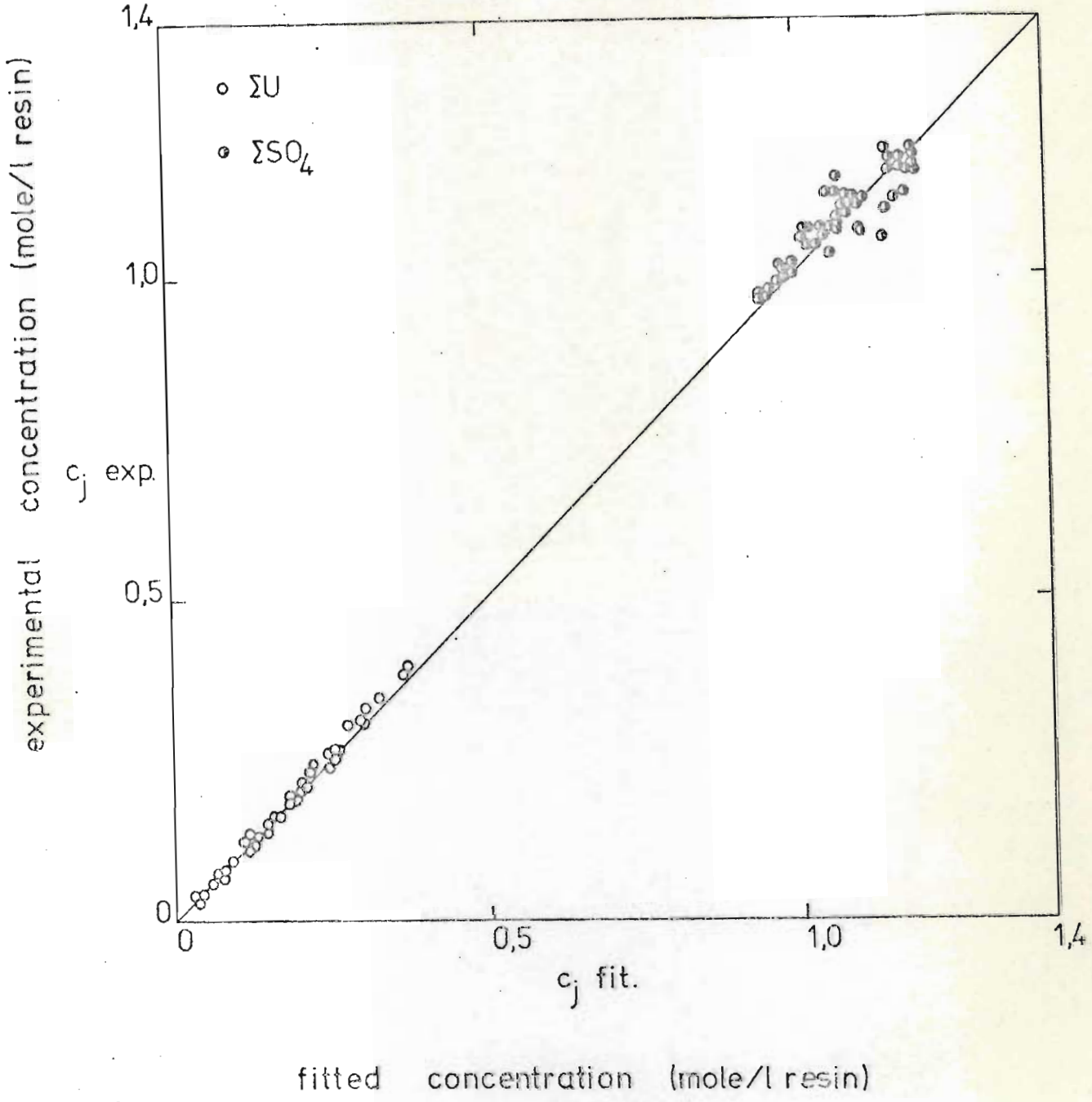


Figure 6.7 Comparison of fitted and experimental concentration on resin for system Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Capacity of 1,4 equiv./l resin used. The Wilson parameters and equilibria constants used are given in Table 6.5. Tabulated data in Appendix Table F.16.

In this work it is assumed that the nitrate exists solely as the NO_3^- anion. The solution phase reactions specified to describe the system are identical to those of the previous quaternary system Equations (6.1) and (6.2).

Extraction of uranium from nitrate media has been reviewed by KORKISH (1970). In nitric acid the absorbility of uranium becomes significant above 2M as reported by BUNNEY *et al* (1959). GOOGIN *et al* (1961), FOREMAN *et al* (1959) and HIGGINS (1961) have reported that the uranium absorption is enhanced in the presence of inorganic nitrates at low acid concentrations.

YOSHIMURA *et al* (1962) indicate that $UO_2(NO_3)_3^-$ is the predominant species in the resin for 2 M external solution nitrate concentration while $UO_2(NO_3)_4^{2-}$ predominates at 4 to 6 M nitrate concentration.

RYAN (1961) has shown that anion exchange resins absorb predominantly the ion $UO_2(NO_s)_4^{2-}$ along with some $UO_2(NO_3)_3^-$ from aqueous metal nitrate solutions (2.0 M $Al(NO_3)_3$). It is also shown that the tetranitrato species does not exist to any appreciable extent in the aqueous phase.

In the extraction of uranium from sulphuric acid leach liquors the nitrate concentration is relatively low. Considering a system or uranyl nitrate, nitric acid and a nitrate salt with a total nitrate concentration of less than 1 M no absorption of uranium is expected. This is checked experimentally for the following six solution conditions.

HNO_3 (M)	0,10	0,10	0,10	0,01	0,01	0,01
$NaNO_3$ (M)	0,20	0,40	0,60	0,20	0,40	0,60
$UO_2(NO_3)_2$ (M)	0,001	0,001	0,001	0,001	0,001	0,001

In all cases no uranium is present on the resin at equilibrium.

This implies that in the application of this approach to uranium extraction from leach liquors no uranyl nitrate complexes are absorbed on the resin and hence the resin and a mixture of uranyl nitrate, nitric acid and sodium nitrate does not constitute a subsystem.

From these considerations the addition of the nitrate ion to the quaternary system previously characterised results in the following two phase reaction scheme.

$$
\begin{aligned}
&R_2SO_4 + 2HSO_4^- \rightleftarrows 2RHSO_4 + SO_4^{2-} \\
&2R_2SO_4 + UO_2SO_4 \rightleftarrows R_4UO_2(SO_4)_3 \\
&R_2SO_4 + UO_2(SO_4)_2^{2-} \rightleftarrows R_2UO_2(SO_4)_2 + SO_4^{2-} \\
&R_2SO_4 + 2NO_3^- \rightleftarrows 2RNO_3 + SO_4^{2-}
\end{aligned}
\qquad (6.9)
$$

The equilibrium constants and quotients have all been defined previously.

It is assumed that the average ligand number ν is not affected by the addition of other non-complexing anions such as NO_3^-.

The equivalent balance equation is given by

$$(2\nu - 2)C_{\Sigma U} + 2C_{SO_4} + C_{HSO_4} + C_{NO_3} = \text{Capacity} \qquad (6.10)$$

and the sulphate mass balance is

$$\nu C_{\Sigma U} + C_{SO4} + C_{HSO_4} = C_{\Sigma SO_4} \qquad (6.11)$$

Combining Equations (6.10) and (6.11) the bisulphate concentration may be inferred from

$$C_{HSO_4} = 2C_{\Sigma SO_4} - \text{Capacity} - 2C_{\Sigma U} + C_{NO_3} \qquad (6.12)$$

A. EXPERIMENTAL

The elution solution is 0,9 N NaCl and 0,1 N HCl. Nitrate concentration is determined as described in Appendix E.5 with corrections for the presence of uranium.

B. RESULTS AND DISCUSSION

The equilibrium compositions of both phases for the system Amberlite 400, mixture Na_2SO_4, $NaNo_3$, H_2SO_4 and UO_2SO_4 at 298^{o}K are summarised in Table 6.6.

The distribution of the various species on the resin is determined as before. Since the total sulphate ion concentration is not required in these calculations this experimental value is available to check the assumptions made in the determination of the bisulphate ion concentration in the resin phase, refer to Appendix Table F.18.

Concentrations of the ionic species in the resin phase are shown in Table 6.7. Equilibrium quotients are calculated from this data converted to mole fractions.

Solution Phase					Resin Phase			
(Mole /ℓ)					(Mole /ℓ Resin)			(Equiv./ℓ Resin)
ΣU	ΣSO_4	ΣH	NO_3	Na	ΣU	ΣSO_4	NO_3	Capacity
0,001	0,251	0,060	0,02	0,46	0,1492	0,7835	0,2857	1,403
0,001	0,251	0,060	0,05	0,49	0,1144	0,6181	0,4914	1,404
0,001	0,251	0,060	0,10	0,54	0,0700	0,4416	0,7257	1,406
0,001	0,251	0,375	0,02	0,145	0,0567	0,9497	0,2685	1,411
0,001	0,251	0,375	0,05	0,175	0,0358	0,7706	0,4857	1,406
0,001	0,251	0,375	0,10	0,225	0,0215	0,5797	0,7428	1,401
0,005	0,255	0,060	0,01	0,450	0,2545	0,9355	0,1314	1,401
0,005	0,255	0,060	0,02	0,460	0,2324	0,8696	0,2343	1,401
0,005	0,255	0,060	0,04	0,480	0,2136	0,7659	0,3657	1,408
0,005	0,255	0,060	0,06	0,500	0,1938	0,6802	0,4629	1,400
0,005	0,255	0,060	0,08	0,520	0,1716	0,6057	0,5686	1,409
0,005	0,255	0,060	0,10	0,540	0,1546	0,5680	0,6314	1,400

Table 6.6 Equilibrium composition of both phases for the system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$, H_2SO_4 and UO_2SO_4, at 298^oK

Resin Phase				
(Mole /ℓ Resin)				
SO_4^*	HSO_4^*	$UO_2(SO_4)_3^*$	$UO_2(SO_4)_2^*$	NO_3
0,2240	0,1770	0,09697	0,05222	0,2857
0,1916	0,1519	0,07434	0,04003	0,4914
0,1607	0,1281	0,04549	0,02449	0,7257
0,1393	0,6769	0,03684	0,01984	0,2685
0,1174	0,5674	0,02325	0,01252	0,4857
0,0866	0,4143	0,01395	0,00751	0,7428
0,1540	0,1218	0,16544	0,08908	0,1314
0,1432	0,1134	0,15109	0,08135	0,2343
0,1208	0,0959	0,13884	0,07476	0,3657
0,1065	0,0847	0,12596	0,06783	0,4629
0,0980	0,0781	0,11155	0,06007	0,5686
0,0923	0,0737	0,10049	0,05411	0,6314

Table 6.7 Experimental resin phase species distribution for the system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$, H_2SO_4 and UO_2SO_4 at 298°K.

This system is characterised with the four interaction coefficients of the Wilson equation related to the ion pair combinations of the nitrate ion and the two uranyl sulphate complexes.

The estimates for these coefficients are presented in Table 6.8. A comparison of the experimental equilibrium quotients and those fitted in the estimation is made in Figures 6,8, 6,9, 6.10 amd 6.11. The root mean square error of the estimates obtained is ± 29.6%.

Application of the parameters estimated from this data leads to fitted resin phase compositions for the solution conditions specified in Table 6.6 which are generally consistent with the experimental values within ± 10% as illustrated in Figure 6.12. However, the experimental value for the total uranium concentration on the resin is generally larger than that calculated.

It is noted that agreement between the fitted and experimental total sulphate concentration on the resin phase is good. This supports the assumptions made in the approach adopted to calculate the bisulphate ion resin phase concentration.

6.1.3 Characterisation of the quinary system SO_4^{2-} - HSO_4^- - $UO_2(SO_4)_3^{4-}$ - $UO_2(SO_4)_2^{2-}$ - Cl

The ion exchange equilibria for the system, Amberlite 400, mixture of Na_2SO_4, H_2SO_4, NaCl and UO_2SO_4 are determined at 298°K.

Both BUNUS (1974) and BANERJEA and TRIPATHI (1961) indicate that a single uranyl chloride complex is formed in the solution phase namely UO_2Cl^+. The cationic complex has a relatively low stability constant of between 1,0 and 2,0.

Λ_{ij}	$UO_2(SO_4)_3$	$UO_2(SO_4)_2$	NO_3	RMS %
$UO_2(SO_4)_3$	1,0	-	1,8904	
$UO_2(SO_4)_2$	-	1,0	3,1197	± 29,6
NO_3	2,9309	0,007278	1,0	

Table 6.8 Estimates of the Wilson interaction coefficients for the system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$, H_2SO_4 and UO_2SO_4 at 298°K. Root mean square error between experimental and fitted equilibrium quotients.

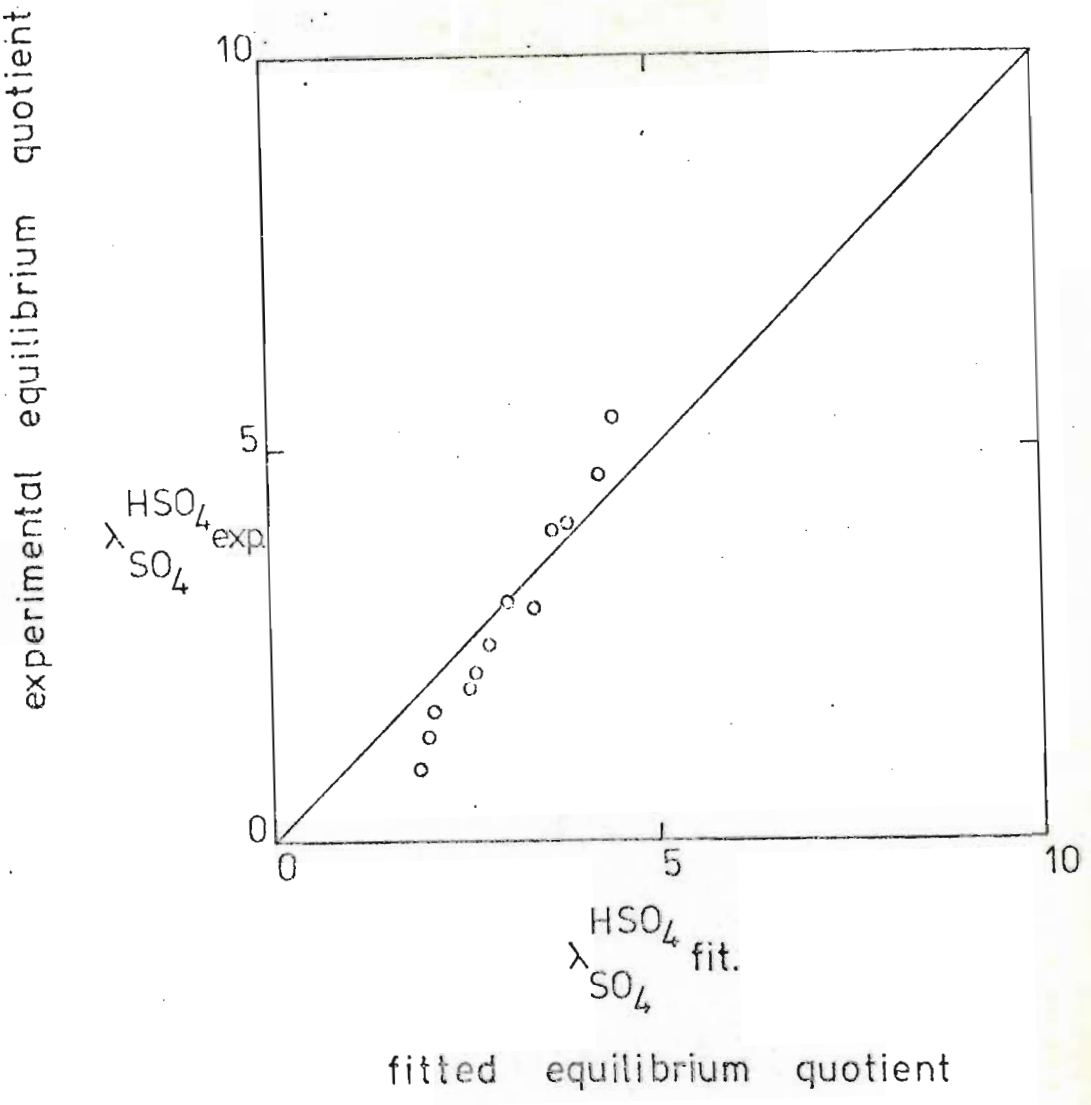


Figure 6.8 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of $NaNO_3$, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Tabulated results in Appendix Table F.17.

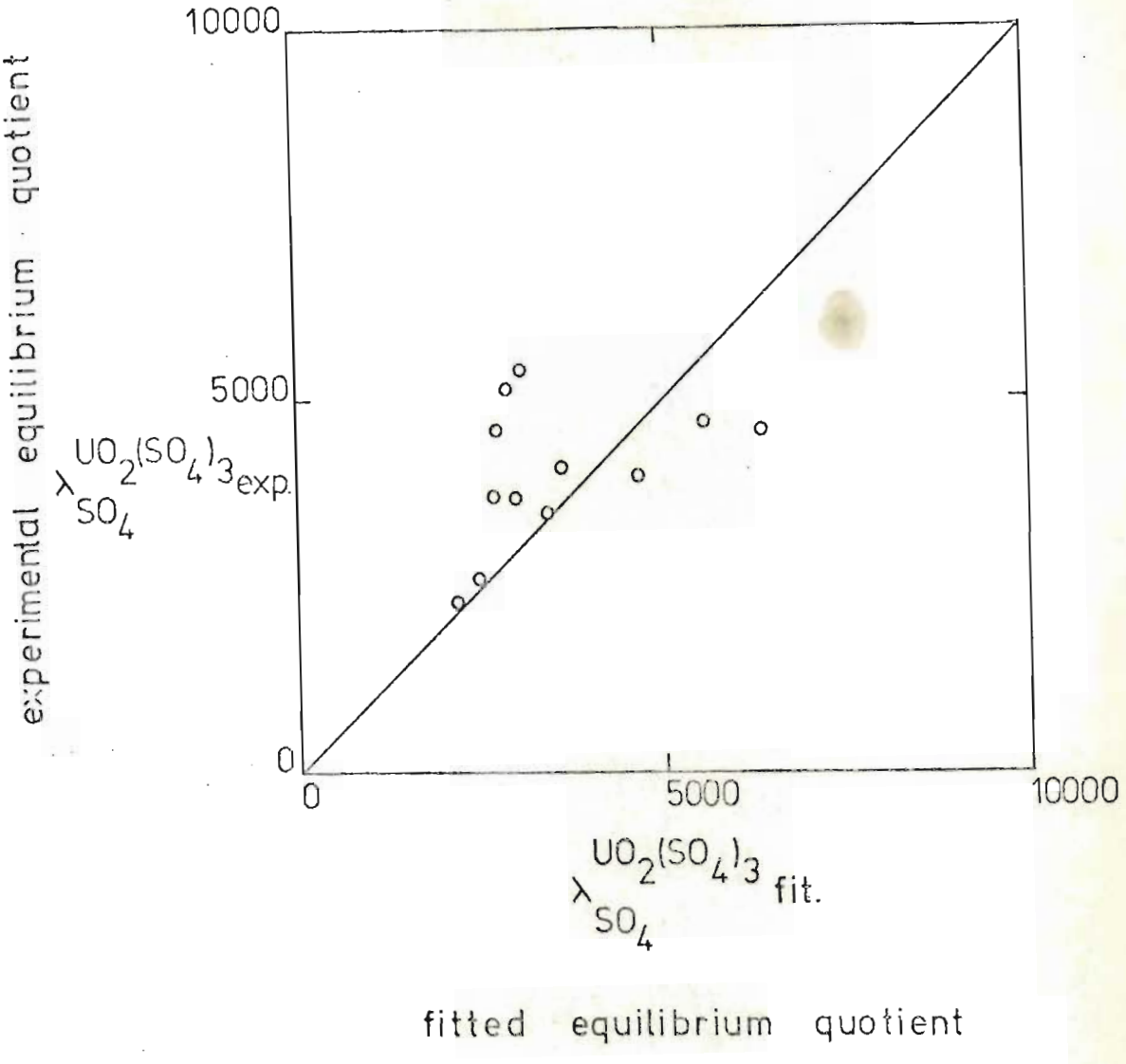


Figure 6.9 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of $NaNO_3$, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Tabulated results in Appendix Table F.17.

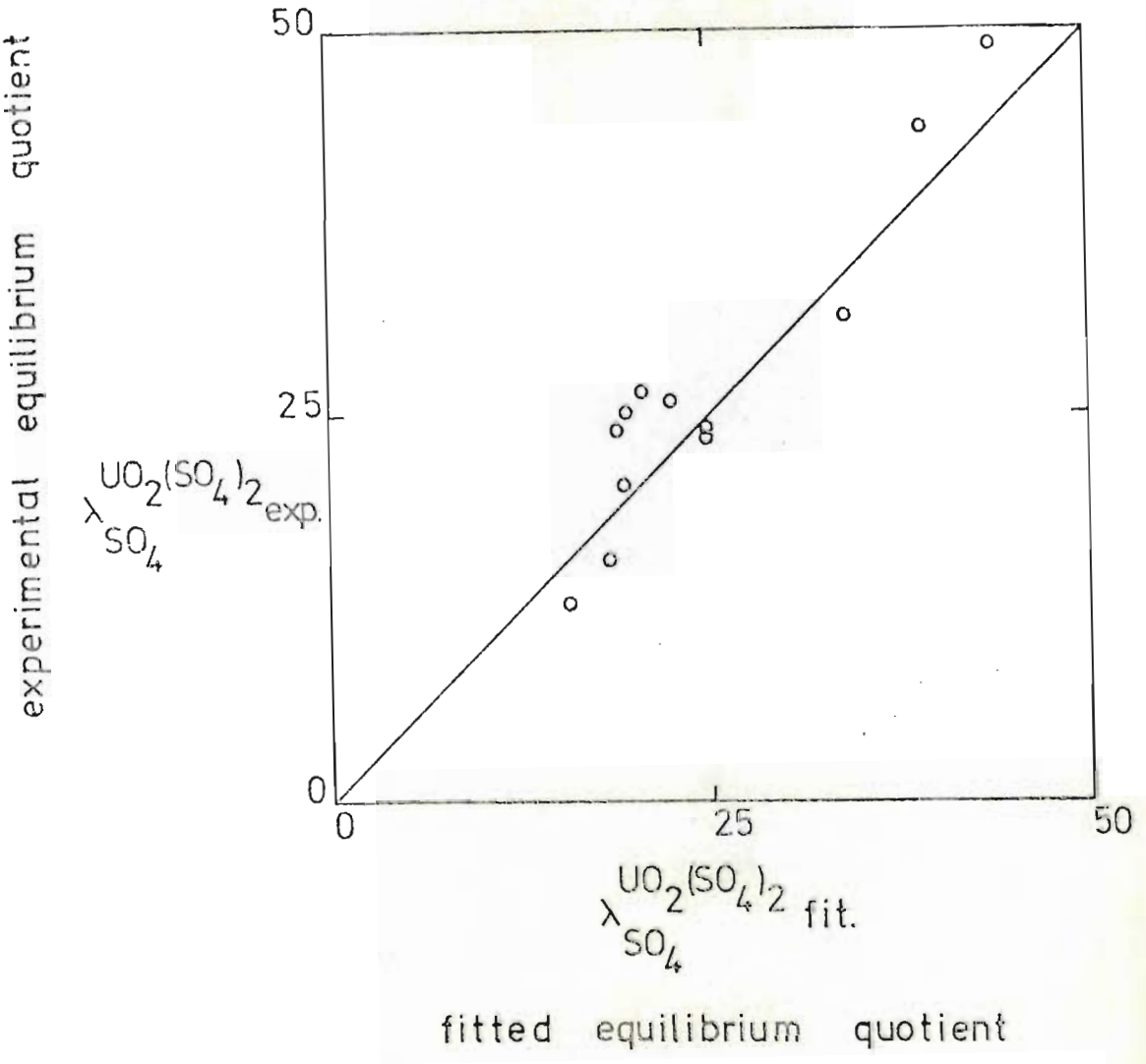


Figure 6.10 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of $NaNO_3$, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Tabulated data Appendix Table F.17.

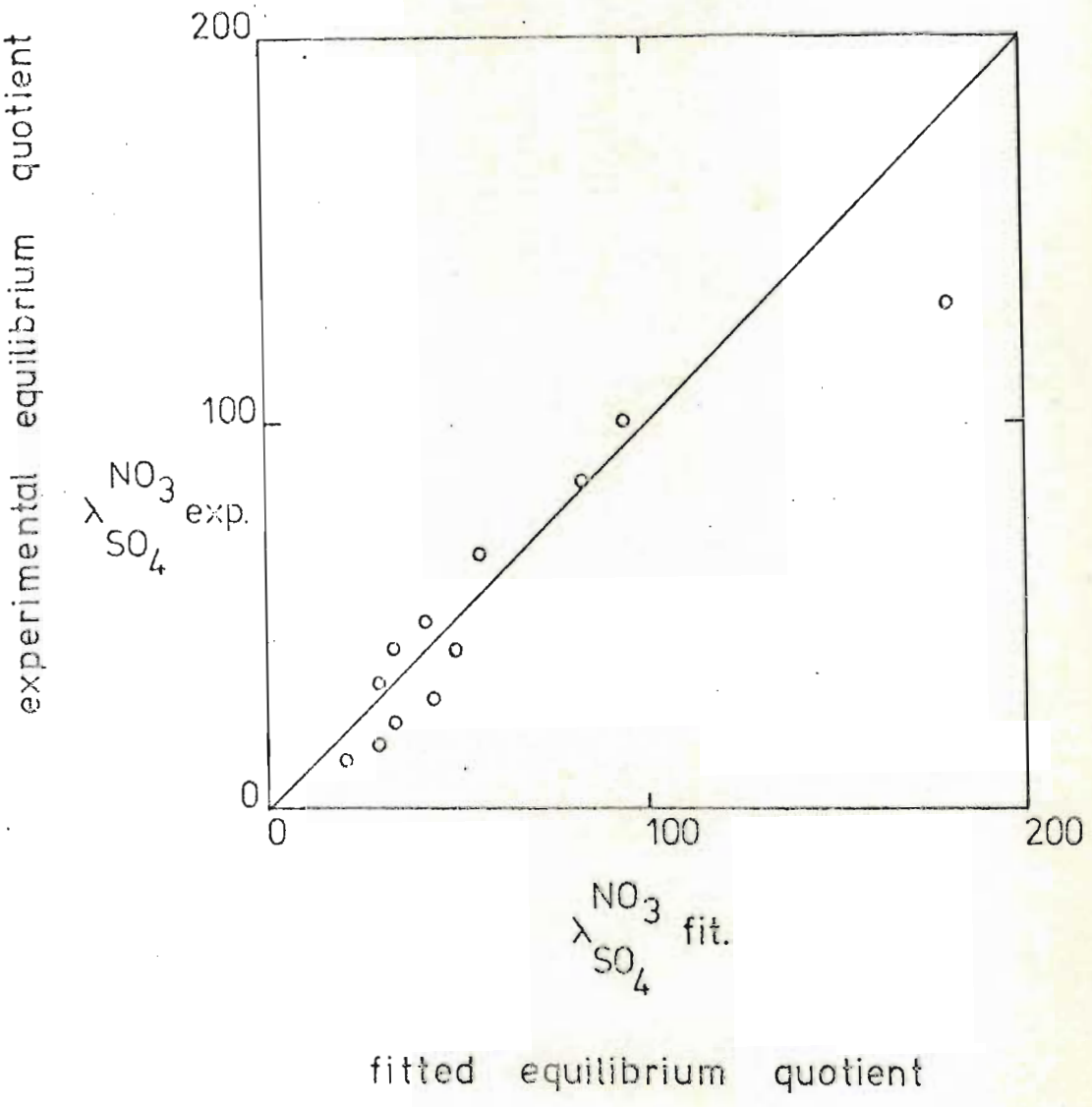


Figure 6.11 Comparison of fitted and experimental equilibrium quotient for system, Amberlite 400, mixture of $NaNO_3$, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Tabulated data in Appendix Table F.17.

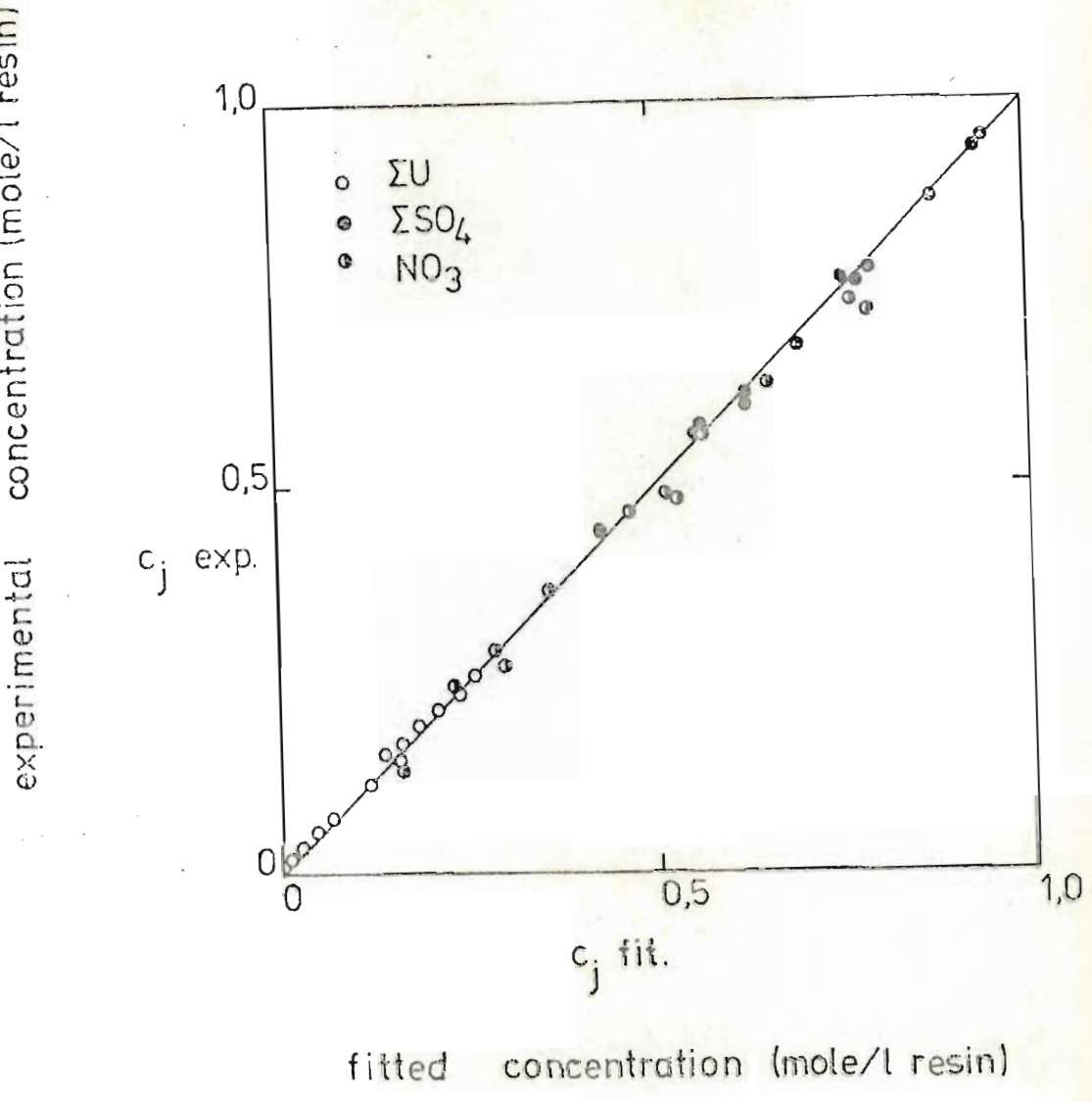


Figure 6.12 Comparison of fitted and experimental concentration on resin for the system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$, H_2SO_4 and UO_2SO_4 at 298°K. Capacity of 1,4 equiv./l resin is used. Tabulated data in Appendix Table F.18.

In this work it is assumed that the chloride exists solely as the Cl^- anion. The solution phase reactions specified to describe this system are identical to those of the quaternary system Equations (6.1) and (6.2).

The extraction of uranium from chloride media has been reviewed by KORKISH (1970). It seems that the chloride concentration has to be very high, 5 to 10 M before the extraction of uranium is significant.

Chloride concentrations in sulphuric acid leach liquors are relatively low and thus no absorption of uranyl chloride complexes is expected. This implies that the system resin, mixture of NaCl, HCl and UO_2Cl_2 is not a subsystem.

Thus the addition of the chloride ion to the quaternary system previously characterised in this chapter results in the following two phase reaction scheme

$$\begin{aligned}
&R_2SO_4 + 2HSO_4^- \rightleftarrows 2RHSO_4 + SO_4^{2-} \\
&2R_2SO_4 + UO_2SO_4 \rightleftarrows R_4UO_2(SO_4)_3 \\
&R_2SO_4 + UO_2(SO_4)_2^{2-} \rightleftarrows R_2UO_2(SO_4)_2 + SO_4^{2-} \\
&R_2SO_4 + 2Cl^- \rightleftarrows 2RCl + SO_4^{2-}
\end{aligned} \qquad (6.13)$$

The equilibrium constants and quotients have been defined previously.

The equivalent balance equation is written as

$$(2\nu - 2)C_{\Sigma U} + 2C_{SO_4} + C_{HSO_4} + C_{Cl} = \text{Capacity} \qquad (6.14)$$

while a sulphate balance is given by

$$\nu C_{\Sigma U} + C_{SO_4} + C_{HSO_4} = C_{\Sigma SO_4} \qquad (6.15)$$

Combining Equations (6.14) and (6.15) the bisulphate concentration may be inferred from

$$C_{HSO_4} = 2C_{\Sigma SO_4} - \text{Capacity} - 2C_{\Sigma U} + C_{Cl} \qquad (6.16)$$

A. EXPERIMENTAL

The elution solution is 0,9 N $NaNO_3$ and 0,1 N HNO_3. Analysis of the chloride, total sulphate, uranium and the capacity are performed as described in Appendix E.

B. RESULTS AND DISCUSSION

The results of the relatively small experimental program for the system Amberlite 400, mixture of Na_2SO_4, NaCl, H_2SO_4 and UO_2SO_4 at 298^{o}K are presented in Table 6.9.

A similar approach to that described in the previous section is applied to determine the distribution of the various species on the resin. In this case the chloride ion is assumed to further reduce the capacity of the resin for sulphate and bisulphate ions. Unfortunately the experimental data required to check this assumption is not available for this system.

Concentrations of the ionic species in the resin phase are shown In Table 6.10. This data converted to mole fractions and the activities of the solution species is used to generate the equilibrium quotients.

Solution Phase					Resin Phase		
(Mole / ℓ)					(Mole / ℓ Resin)		(Equiv/ℓ Resin)
ΣU	ΣSO_4	ΣH	Cl	Na	ΣU	Cl	Capacity
0,001	0,251	0,060	0,010	0,450	0,1854	0,0508	1,400
0,001	0,251	0,060	0,025	0,465	0,1730	0,1036	1,400
0,001	0,251	0,060	0,050	0,490	0,1639	0,1916	1,400
0,001	0,251	0,060	0,100	0,540	0,1322	0,3472	1,400
0,001	0,251	0,060	0,150	0,590	0,1056	0,4956	1,400
0,001	0,251	0,060	0,200	0,640	0,0819	0,6188	1,400
0,005	0,255	0,060	0,010	0,450	0,2710	0,0376	1,400
0,005	0,255	0,060	0,025	0,465	0,2616	0,0756	1,400
0,005	0,255	0,060	0,050	0,490	0,2359	0,1392	1,400
0,005	0,255	0,060	0,100	0,540	0,2087	0,2604	1,400
0,005	0,255	0,060	0,150	0,590	0,1894	0,3812	1,400
0,005	0,255	0,060	0,200	0,640	0,1762	0,4820	1,400

Table 6.9 Equilibrium composition of both phases for system Amberlite 400, mixture of Na_2SO_4 , NaCl, H_2SO_4 and UO_2SO_4 at 298°K.

Resin Phase				
(Mole /ℓ Resin)				
SO_4^*	HSO_4^*	$UO_2(SO_4)_3^*$	$UO_2(SO_4)_2^*$	Cl
0,2644	0,2087	0,12051	0,06489	0,0508
0,2597	0,2061	0,11246	0,06056	0,1036
0,2390	0,1895	0,10655	0,05738	0,1916
0,2205	0,1757	0,08590	0,04626	0,3472
0,1985	0,1589	0,06865	0,03697	0,4956
0,1822	0,1465	0,05325	0,02867	0,6188
0,1677	0,1327	0,17615	0,09485	0,0376
0,1651	0,1308	0,17005	0,09156	0,0756
0,1726	0,1371	0,15333	0,08257	0,1392
0,1612	0,1287	0,13564	0,07303	0,2604
0,1405	0,1127	0,12311	0,06629	0,3812
0,1200	0,0967	0,11450	0,06166	0,4820

Table 6.10 Experimental resin phase species distribution for system Amberlite 400, mixture of Na_2SO_4, NaCl, H_2SO_4 and UO_2SO_4 at 298°K.

Only four parameters are estimated from this data namely the interaction coefficients for the ion pair combinations of the chloride ion and the two uranyl sulphate complexes. The estimates for these coefficients are presented in Table 6.11. A comparison of the experimental equilibrium quotients and those fitted in the estimation is made in Figures 6.13, 6.14, 6.15 and 6.16. The root mean square error of the estimates obtained is ± 14,6%.

Although the differences between the experimental and fitted equilibrium quotients are large in some cases, application of the parameters estimated from this data leads to fitted resin phase compositions for the solution conditions stated in Table 6.9 which are consistent with the experimental values within ± 5%. This is illustrated in Figure 6.17. The measureable quantities are significantly less sensitive than the equilibrium quotients.

6.2 PREDICTION OF THE SIX COMPONENT SYSTEM

$$SO_4^{2-} - HSO_4^- - UO_2(SO_4)_3^{4-} - UO_2(SO_4)_2^{2-} - NO_3^- - Cl^-$$

The charcteristics of the following subsystems allow the prediction of the equilibrium resin phase composition of this six component system.

Binary systems

$$SO_4^{2-} - NO_3^-, \quad SO_4^{2-} - Cl, \quad SO_4^{2-} - HSO_4^-, \quad NO_3^- - Cl^-$$

Ternary systems,

$$SO_4^{2-} - HSO_4^- - Cl^-, \quad SO_4^{2-} - HSO_4^- - NO_3^-$$

Λ_{ij}	$UO_2(SO_4)_3$	$UO_2(SO_4)_2$	Cl	RMS %
$UO_2(SO_4)_3$	1,0	-	0,23027	
$UO_2(SO_4)_2$	-	1,0	0,049312	± 14,6
Cl	4,9292	2,4865	1,0	

Table 6.11 Estimates of the Wilson interaction coefficients for the system Amberlite 400, mixture of Na_2SO_4, NaCl, H_2SO_4 and UO_2SO_4 at 298°K. Root mean square error between experimental and fitted equilibrium quotients.

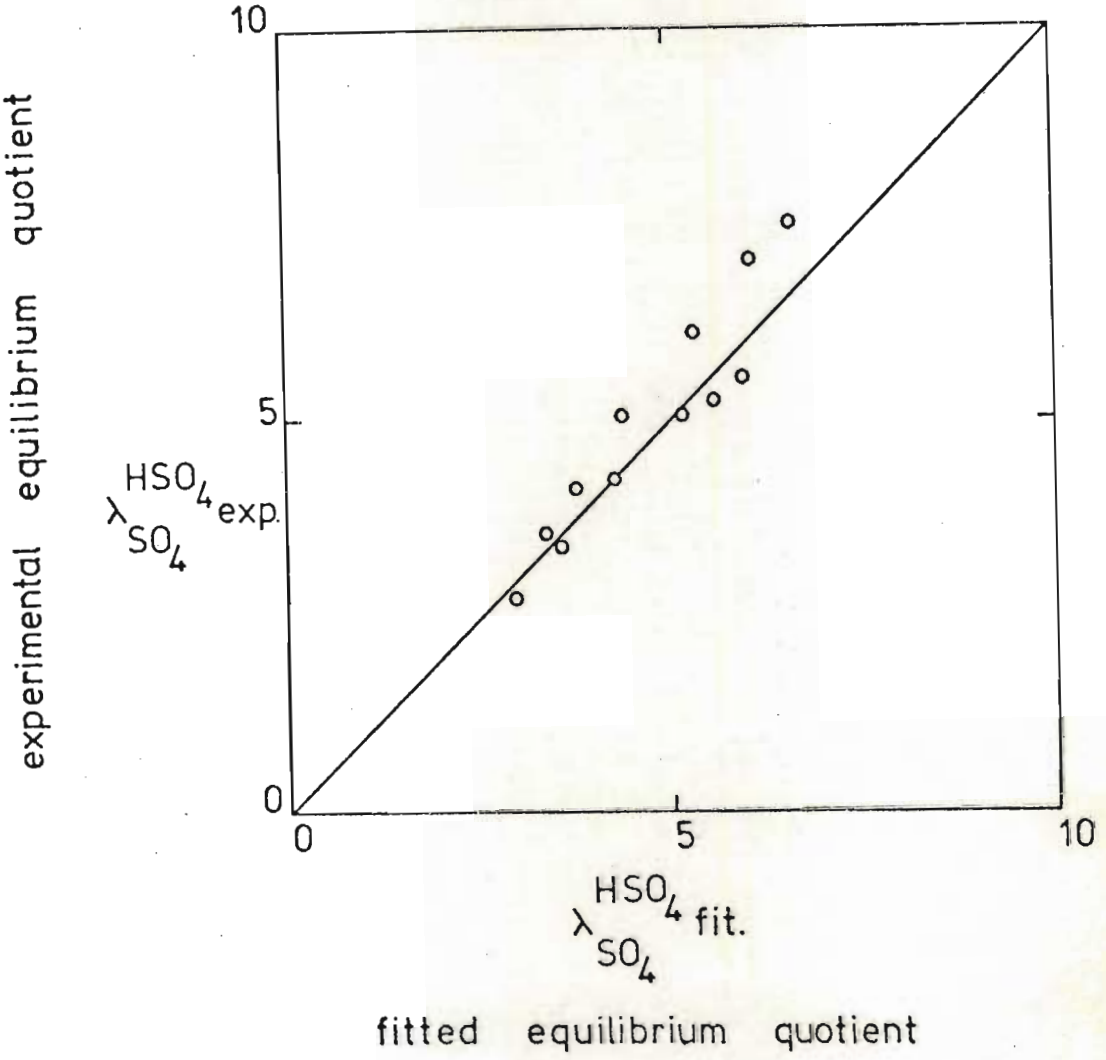


Figure 6.13 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of NaCl, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Tabulated data in Appendix Table F.19.

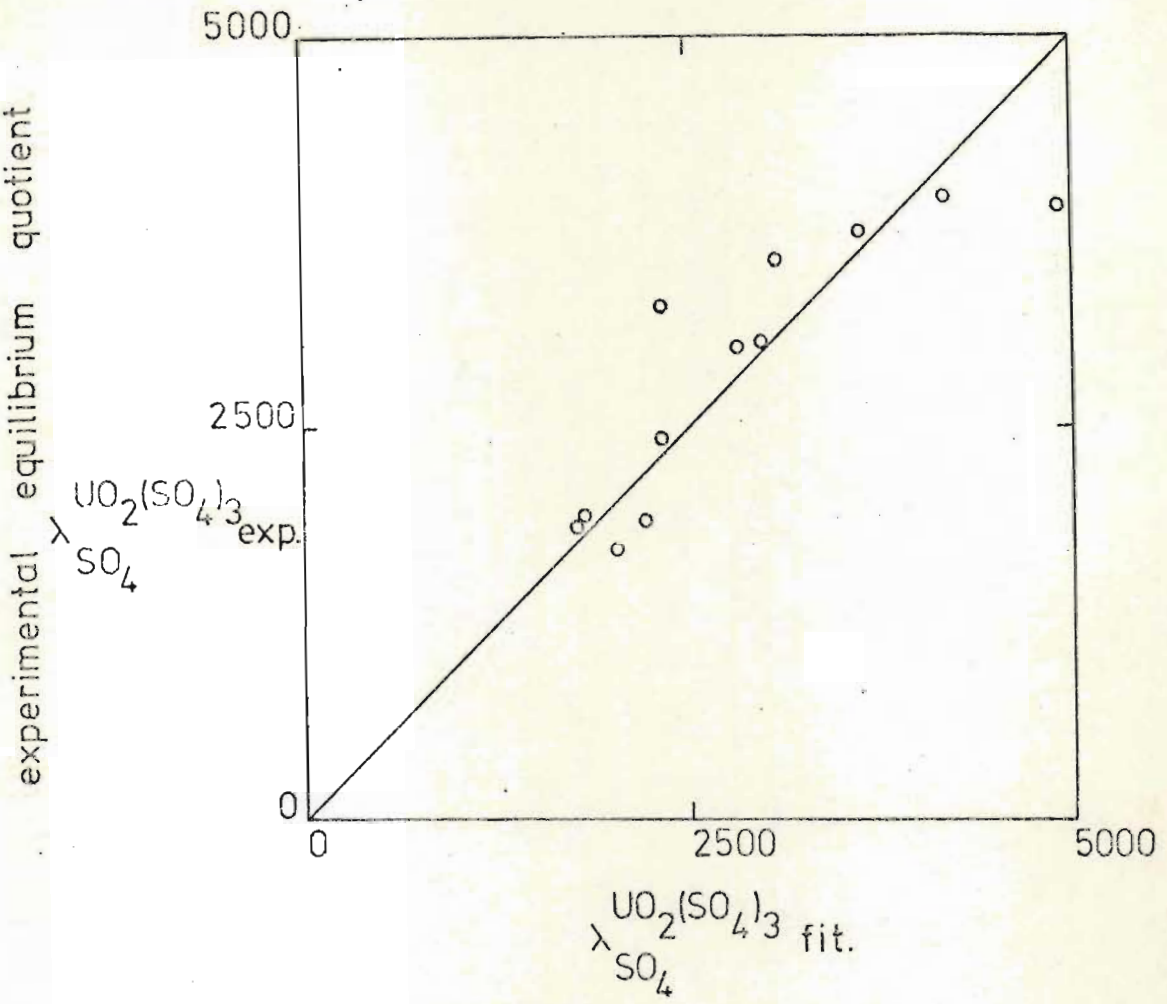


Figure 6.14 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of NaCl, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Tabulated data in Appendix Table F.19.

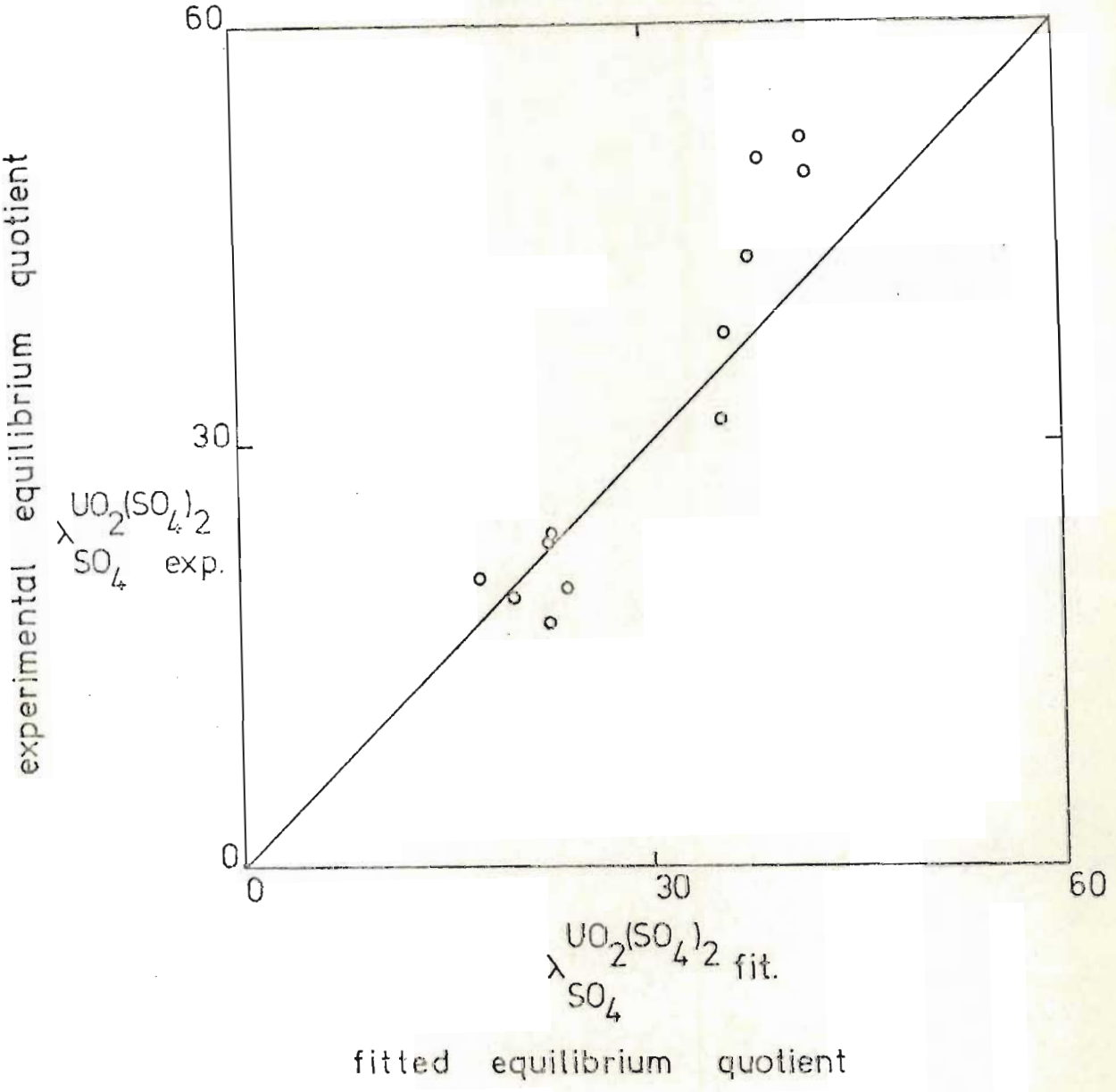


Figure 6.15 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of NaCl, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K.
Tabulated data in Appendix Table F.19.

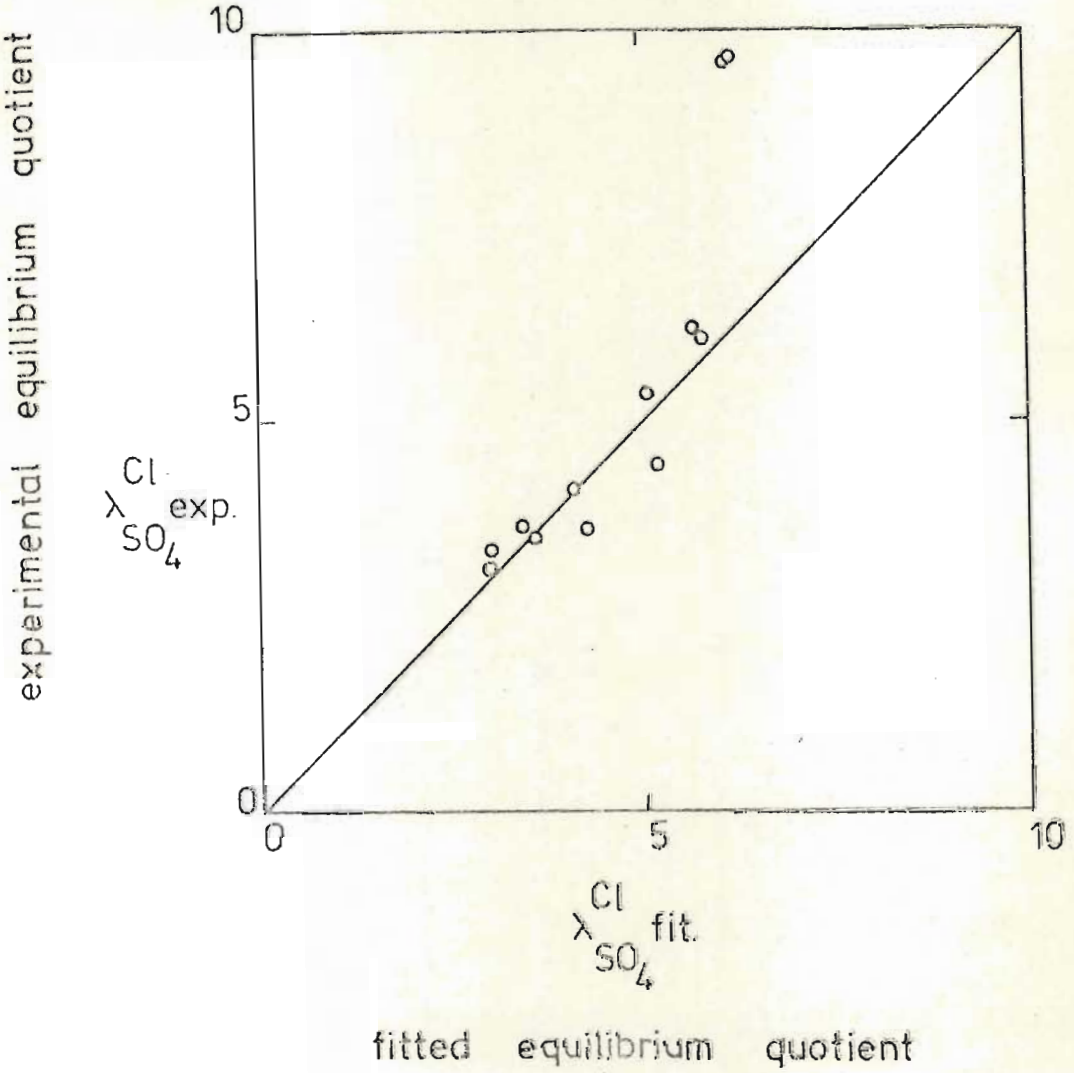


Figure 6.16 Comparison of fitted and experimental equilibrium quotient for system Amberlite 400, mixture of NaCl, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Tabulated data in Appendix Table F.19.

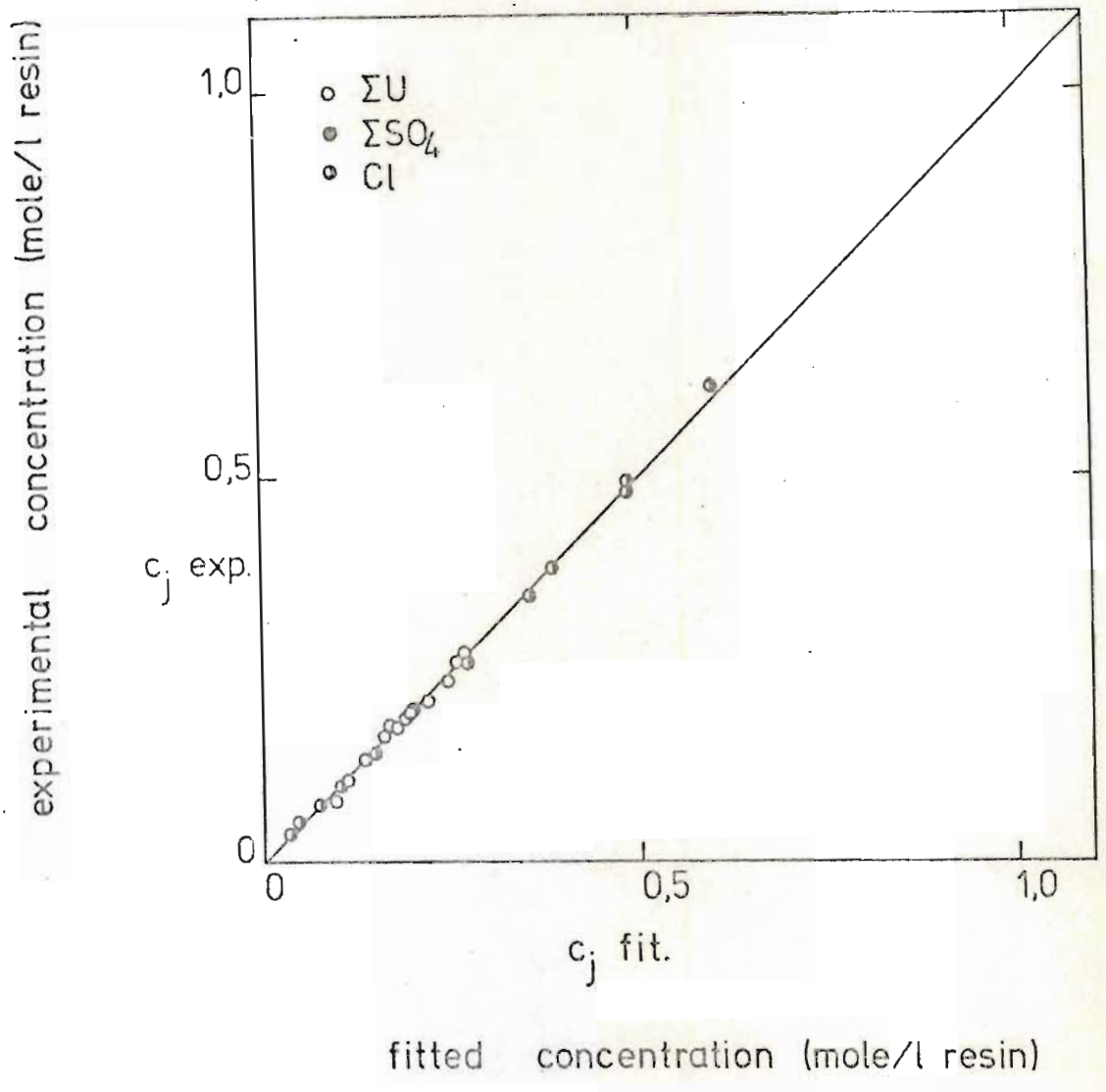


Figure 6.17 Comparison of fitted and experimental concentration on resin for system Amberlite 400, mixture of Na_2SO_4, NaCl, H_2SO_4 and UO_2SO_4 at 298°K. Capacity is 1,4 equiv./l resin. Tabulated data in Appendix Table F.20.

Quaternary systems

$$SO_4^{2-} - HSO_4^- - UO_2(SO_4)_3^{4-} - UO_2(SO_4)_2^{2-}$$

Quinary systems,

$$SO_4^{2-} - HSO_4^- - UO_2(SO_4)_3^{4-} - UO_2(SO_4)_2^{2-} - NO_3,$$

$$SO_4^{2-} - HSO_4^- - UO_2(SO_4)_3^{4-} - UO_2(SO_4)_2^{2-} - Cl$$

The interaction parameters and the equilibrium constants estimated for these subsystems are combined through the Wilson equation to predict the equilibrium resin phase composition and activity coefficient for the solution conditions specified in Table 6.14.

The set of independent heterogeneous equilibrium reactions required to describe this system is

$$R_2SO_4 + 2HSO_4^- \rightleftarrows 2RHSO_4 + SO_4^{2-}$$

$$2R_2SO_4 + UO_2SO_4 \rightleftarrows R_4UO_2(SO_4)_3$$

$$R_2SO_4 + UO_2(SO_4)_2^{2-} \rightleftarrows R_2UO_2(SO_4)_2 + SO_4^{2-} \qquad (6.17)$$

$$R_2SO_4 + 2NO_3^- \rightleftarrows 2RNO_3 + SO_4^{2-}$$

$$R_2SO_4 + 2Cl^- \rightleftarrows 2RCl + SO_4^{2-}$$

The solution phase reactions are

$$H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$$

$$UO_2^{2+} + SO_4^{2-} \rightleftarrows UO_2SO_4$$

$$UO_2^{2+} + 2SO_4^{2-} \rightleftarrows UO_2(SO_4)_2^{2-} \qquad (6.18)$$

$$Na^+ + SO_4^{2-} \rightleftarrows NaSO_4^-$$

The equilibrium constants for the heterogeneous reactions are summarised in Table 6.12. The interaction coefficients required are reported in Table 6.13. A capacity of 1,4 equivalents per litre of free settled resin is assumed in the predictions.

Specimen calculations of the activity of the solution species and the prediction of the resin phase composition are given in the Appendixes J.2.1.A and J.2.1.C respectively for the first experimental condition of Table 6.14.

6.2.1 Test experiments of the six component system $SO_4^{2-} - HSO_4^- - UO_2(SO_4)_3^{4-} - UO_2(SO_4)_2^{2-} - NO_3^- - Cl^-$ for comparison with the predicted compositions

Ion exchange equilibria are determined for the system, Amberlite 400, 0,4 N mixture of Na_2SO_4, H_2SO_4, NaCl, $NaNO_3$ and UO_2SO_4 at 298°K.

The equivalent balance equation for the resin phase is expressed as

$$(2\nu - 2)C_{\Sigma U} + 2C_{SO_4} + C_{HSO_4} + C_{NO_3} + C_{Cl} = \text{Capacity} \qquad (6.19)$$

Ion Exchange Reaction	Equilibrium Constant
$R_2SO_4 + 2H\,SO_4^- \rightleftarrows 2RHSO_4 + SO_4^{2-}$	$K_{SO_4}^{HSO_4} = 5,098$
$2R_2SO_4 + UO_2SO_4 \rightleftarrows R_4UO_2(SO_4)_3$	$K_{SO_4}^{UO_2(SO_4)_3} = 7381,8$
$R_2SO_4 + UO_2(SO_4)_2^{2-} \rightleftarrows R_2UO_2(SO_4)_2 + SO_4^{2-}$	$K_{SO_4}^{UO_2(SO_4)_2} = 41,408$
$R_2SO_4 + 2NO_3^- \rightleftarrows 2RNO_3 + SO_4^{2-}$	$K_{SO_4}^{NO_3} = 72,939$
$R_2SO_4 + 2Cl^- \rightleftarrows 2RCl + SO_4^{2-}$	$K_{SO_4}^{Cl} = 5,104$

Table 6.12 Summary of the ion exchange reactions and equilibrium constants at 298°K used to predict the resin phase composition of the six component system Amberlite 400, 0,4 N mixture of Na_2SO_4, NaCl, $NaNO_3$, H_2SO_4 and UO_2SO_4.

Λ_{ij}	SO_4	HSO_4	$UO_2(SO4)_3$	$UO_2(SO_4)_2$	NO_3	Cl
SO_4	1,0	0,9846	4,8276	5,2322	0,65419	0,21192
HSO_4	2,8124	1,0	2,8237	0,81317	2,6912	0,74146
$UO_2(SO_4)_3$	0,0026155	0,62344	1,0	0,036596	1,8904	0,23027
$UO_2(SO_4)_2$	1,7304	0,85263	1,7655	1,0	3,1197	0,049312
NO_3	3,1159	0,27678	2,9309	0,007278	1,0	0,39121
Cl	3,7355	1,2865	4,9292	2,4865	2,4627	1,0

Table 6.13 Summary of the Wilson interaction coefficients at 298°K used to predict the resin phase activity coefficients of the six component system Amberlite 400, 0,4 N mixture of Na_2SO_4, NaCl, $NaNO_3$, H_2SO_4 and UO_2SO_4.

A mass balance for sulphate species in the resin phase is given by

$$\nu C_{\Sigma U} + C_{SO_4} + C_{HSO_4} = C_{\Sigma SO_4} \qquad (6.20)$$

A. EXPERIMENTAL

A total solution concentration of 0,4 N was selected for this system. If the total chloride and nitrate concentrations of the solution are specified then the total sulphate concentration is fixed from an equivalent balance. Further, if the total uranium concentration and the ratio δ of the hydrogen ion to the total sulphate conentration are specified then the four independent variables total chloride, nitrate, uranium and δ may be used to design a two level experiment.

The values selected for these variables are

total chloride equivalent fraction	0,1 and 0,3
total nitrate equivalent fraction	0,05 and 0,2
Total uranium concentration (M)	0,001 and 0,005
ratio δ	0,8 and 0,2.

Two further tests were run as duplicate experiments at conditions similar to those expected in an industrial situation.

6.2.2 Results and discussion

The results of the test experiments and predictions are summarised in Table 6.14 and Figure 6.18.

Solution Phase (Mole / ℓ)						Resin Phase (Mole / ℓ Resin) Experimental				Predicted			
ΣU	ΣSO_4	ΣH	NO_3	Cl	Na	ΣU	ΣSO_4	NO_3	Cl	ΣU	ΣSO_4	NO_3	Cl
0,001	0,140	0,112	0,080	0,040	0,286	0,0444	0,4146	0,732	0,1139	0,0361	0,3962	0,7674	0,1205
0,001	0,140	0,028	0,080	0,040	0,370	0,0764	0,3461	0,716	0,1135	0,0655	0,3603	0,7485	0,1213
0,001	0,170	0,136	0,020	0,040	0,262	0,1038	0,7008	0,280	0,1431	0,0920	0,7242	0,3049	0,1490
0,001	0,170	0,034	0,020	0,040	0,364	0,1441	0,6597	0,288	0,1407	0,1442	0,6684	0,2940	0,1458
0,001	0,100	0,080	0,080	0,120	0,318	0,0325	0,2536	0,696	0,3268	0,0215	0,2448	0,7355	0,3374
0,001	0,100	0,020	0,080	0,120	0,378	0,0495	0,2313	0,680	0,3244	0,0372	0,2214	0,7279	0,3387
0,001	0,130	0,104	0,020	0,120	0,294	0,0676	0,5157	0,266	0,4144	0,0670	0,5156	0,2948	0,4202
0,001	0,130	0,026	0,020	0,120	0,372	0,1047	0,5106	0,270	0,4059	0,1031	0,4858	0,2843	0,4095
0,005	0.140	0,112	0,080	0,040	0,278	0,1196	0,4592	0,596	0,0923	0,0984	0,4971	0,6631	0,1041
0,005	0,140	0,028	0,080	0,040	0,362	0,1613	0,5654	0,576	0,0874	0,1393	0,5027	0,6193	0,0985
0,005	0,170	0,136	0,020	0,040	0,254	0,1791	0,8516	0,236	0,1072	0,1756	0,8051	0,2563	0,1189
0,005	0,170	0,034	0,020	0,040	0,356	0,2311	0,7984	0,228	0,1008	0,2239	0,7790	0,2414	0,1099
0,005	0,100	0,080	0,080	0,120	0,310	0,0903	0,4609	0,608	0,2807	0,0680	0,3341	0,6646	0,3047
0,005	0,100	0,020	0,080	0,120	0,370	0,1241	0,4592	0,588	0,2637	0,0968	0,3494	0,6309	0,2920
0,005	0,130	0,104	0,020	0,120	0,286	0,1575	0,7145	0,228	0,3337	0,1405	0,6203	0,2540	0,3486
0,005	0,130	0,026	0,020	0,120	0,364	0,1832	0,7349	0,224	0,3114	0,1793	0,6190	0,2396	0,3244
0,005	0,184	0,092	0,012	0,02	0,298	0,2211	0,9224	0,072	0,0586	0,2234	0,8918	0,1762	0,0591
0,005	0,184	0,092	0,012	0,02	0,298	0,2321	0,9106	0,072	0,0586	0,2234	0,8918	0,1762	0,0591

Table 6.14 Comparison of experimental and predicted equilibrium composition of the resin phase for the system Amberlite 400, 0,4 N mixture of Na_2SO_4, $NaNO_3$, NaCl, H_2SO_4 and UO_2SO_4 at 298°K. Capacity of resin is 1,4 equiv./l resin. This data is presented graphically in Figure 6.18.

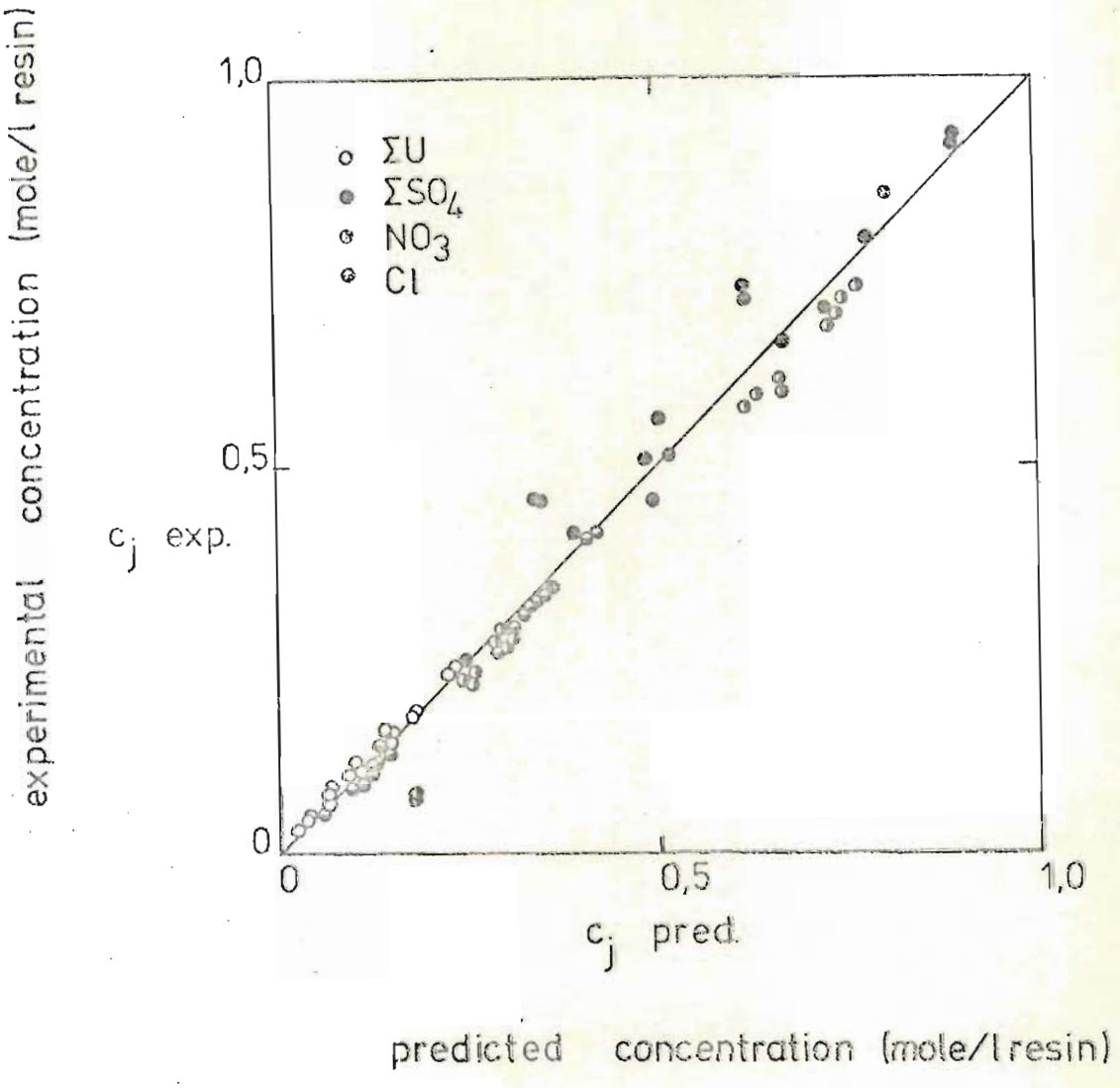


Figure 6.18 Comparison of predicted and experimental concentration on resin for system Amberlite 400, 0,4 N mixture of NaCl $NaNO_3$, Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Capacity is 1,4 equiv./l resin. Tabulated data in Table 6.14.

The predictions of the resin phase are presented as the corresponding experimentally measurable quantity for comparison with the measured data although the prediction procedure gives the distribution of all the six components in the resin phase.

It may be seen that the predicted results are consistent with the experimental data over a moderately large resin phase composition range.

$$0{,}03 < C_{\Sigma U} < 0{,}23$$

$$0{,}23 < C_{\Sigma SO_4} < 0{,}92$$

$$0{,}07 < C_{NO_3} < 0{,}73$$

$$0{,}06 < C_{Cl} < 0{,}41$$

In general agreement between predicted and experimental data is within ± 10%. The final two experiments in Table 6.14 are duplicate tests from which it may be seen that good reproducibility is possible. The low values for the experimental nitrate concentration for these tests are ascribed to analytical error since in these samples the uranium concentration, which interferes with the nitrate analysis, is sufficiently high to make the U.V. absorption due to uranium approximately equal to that of the nitrate alone.

The duplicate tests have nitrate and chloride ion solution concentrations similar to those in typical leach liquors. It is noted that these low solution concentrations result in significant nitrate and chloride being absorbed by the resin thereby depressing the uranium loading.

In general the experimental values of the total uranium concentration on the resin are greater than the predicted values, particularly when the nitrate concentration is relatively large. This discrepancy may be due to the less accurate characterisation of the quinary system SO_4^{2-} - HSO_4^- - $UO_2(SO_4)_3^{4-}$ - $UO_2(SO_4)_2^{2-}$ - NO_3^- which exhibited similar errors.

Nevertheless the results of this system are very encouraging in that the procedure presented has predicted the extent of most of the well known qualitative observations in uranium extraction with ion exchangers. Ferric ion, a very important component in industrial schemes, has been neglected only through lack of information regarding the complexing in the resin phase.

In the same way the reaction scheme presented in this work is limited in application to the solution region-

$C'_{\Sigma SO_4} < 1$ M

$C'_{NO_3} < 1$ M

$C'_{Cl} < 1$ M

$C'_{\Sigma U} < 0,1$ M

pH < 2,5

Ignoring the ferric ion this region encompasses most sulphuric acid leach liquors.

Clearly the practical application of this system is dependent on the ferric ion concentration and the future characterisation of ferric complex systems.

CHAPTER SEVEN

CONCLUSIONS AND SIGNIFICANCE

It has been shown that it is possible to predict multicomponent ion exchange system equilibria from the combination of characteristics of subsystems generated by the decomposition of the complex multiionic system.

The characteristics are ion exchange reaction equilibrium constants and binary ionic interaction coefficients of the Wilson equation.

The major advantage of this approach is the large reduction in the experimental effort required to describe a multicomponent system.

Binary and higher order subsystems considered in this work have been successfully characterised by the Wilson model and the ion exchange reaction equilibrium constants.

The general scheme proposed for the prediction of multicomponent ion exchange problems has been very successfully applied to the simple ternary system SO_4^{2-} - NO_3^- - Cl^-, the quaternary system SO_4^{2-} - HSO_4^- - NO_3^- - Cl^- which illustrates the difficulties associated with introducing ionic complexes into the resin phase of the system; and the six component system SO_4^{2-} - HSO_4^- - $UO_2(SO_4)_3^{4-}$ - $UO_2(SO_4)_2^{2-}$ - NO_3^- - Cl^- with three complex ions in the resin phase.

Ionic complexes in the resin phase do not present a problem provided the stoichiometry of the complexes are established, however they do increase the order of the subsystems generated by the decomposition of a complex multiionic system.

Non-idealities in the two phases are dealt with separately. The solution phase activity coefficients have been approximated using the extended Debye-Huckel equation. For the conditions considered, this approach is shown to be sufficiently accurate.

Incorporating non-idealities of the solution phase in the model allows predictions to be made at various solution normalities for various supporting electrolytes.

The charcterisation of the subsystem has quantified the non-idealities in the resin phase.

Application of the scheme to a particular multicomponent ion exchange system requires the binary ion exchange and aqueous phase complex reaction equilibrium constants, parameters for the resin phase non-idealities, parameters for the aqueous phase non-idealities and the initial conditions of the solution and resin phases.

Within certain constraints the proposed scheme has successfully predicted the influence that the solution phase characteristics have on the uranium loading from a pure solution related to the typical leach liquor. Most of the qualitative observations reported before concerning the effects that the solution composition has on the extraction of uranium from sulphuric acid leach liquors may now be quantitatively predicted.

Ferric ion has been neglected from the systems investigated because the complex species of this metal ion with ligands particularly in the resin phase have yet to be adequately described and quantitatively measured.

This species has a significant role to play in the performance of an ion exchange system for the recovery of uranium from acid leached ore bodies and as such should be included in the reaction scheme before useful predictions of the industrial system may be expected.

CHAPTER EIGHT

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APPENDIX A

EQUILIBRIUM CONSTANTS AND PARAMETERS FOR THE SOLUTION PHASE

A.1 Equilibrium constant of complex species in aqueous solutions

The major compilations of stability constant data are due to SILLEN and MARTELL (1964), GARRELS and CHRIST (1965) and RINGBOM (1963). FINKELSTEIN and NEEDES (1971) have reviewed and compiled a table of the stability constants for the uranium sulphate system.

Table A.1 provides a summary of the stability constants considered in the calculations.

All the values quoted are at 298°K and at zero ionic strength.

The general expression for the stability constant as applied in the calculations is:

$$K_n = \frac{(M\,L_n)}{(M)\,(L)^n}$$

where $(M\,L_n)$, (M), (L) are activities of the species, M refers to the central atom, L refers to the ligand and ML_n denotes the complex.

A.2 Parameters for the extended Debye-Huckel equation at 298°K

Table A.2 provides a summary of the parameters related to each aqueous species considered in the system for the determination of the activity coefficient from the equation:

$$\ln \gamma_j = \frac{-A\, z_j^2 \sqrt{I}}{1 + Ba_j \sqrt{I}} + b_j I$$

$A = 0,5085$

$B = 0,3281 \times 10^8$

Species j	Reaction	Stability Constant K	Reference
HSO_4^-	$H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$	91,20	SILLEN AND MARTELL (1964)
UO_2SO_4	$UO_2^{2+} + SO_4^{2-} \rightleftarrows UO_2\ SO_4$	1380,4	WALLACE (1967)
$UO_2\ (SO_4)_2^{2-}$	$UO_2^{2+}\ 2SO_4^{2-} \rightleftarrows UO_2\ (SO_4)_2^{2-}$	16218,0	WALLACE (1967)
$Na\ SO_4^-$	$Na^+ + SO_4^{2-} \rightleftarrows Na\ SO_4^-$	5,248	SILLEN AND MARTELL (1964)

Table A.1 Stability constants of the complexes for the aqueous systems considered in this work at 298°K and zero ionic strength.

Species j	z_j	$a_j \times 10^{-8}$	b_j	Reference
H^+	+1	9,0	0,0	TRUESDELL AND JONES (1973)
SO_4^{2-}	-2	5,0	-0,04	TRUESDELL AND JONES (1973)
HSO_4^-	-1	4,5	0,0	TRUESDELL AND JONES (1973)
UO_2^{2+}	+2	6,0	0,0	WALLACE (1967)
$UO_2\ SO_4$	0	0,0	0,0	WALLACE (1967)
$UO_2\ (SO_4)_2^{-2}$	-2	6,0	0,0	WALLACE (1967)
Na^+	+1	4,0	0,075	TRUESDELL AND JONES (1973)
$Na\ SO_4^-$	-1	5,4	0,0	TRUESDELL AND JONES (1973)
NO_3^-	-1	3,0	0,0	TRUESDELL AND JONES (1973)
Cl^-	-1	3,5	0,015	TRUESDELL AND JONES (1973)

Table A.2 Parameters for the extended Debye - Huckel Equation

APPENDIX B

DESCRIPTION OF APPARATUS

B.1 CONTACT CELLS

The glass contact cells consist of resin holders and inlet and outlet sections as shown in Figure B.1a. Materials of construction are glass Quickfit B24 joints and sintered glass discs of porosity No. 2. Each resin holder is designed to hold approximately 10 ml of ion exchange resin beads in a column which has dimensions compatible with those of the centrifuge tubes used as shown in Figure B.1b.

B.2 Proportioning pumps

Six proportioning pumps with a single drive unit feed the various solutions to the contact cells as indicated in Figure B.2. Flowrates may be adjusted between 0 and 230 ml/hr.

B.3 Centrifuge

A MSE minor centrifuge with automatic timer and speed control is used for the separation of the liquid from the ion exchange resin beads.

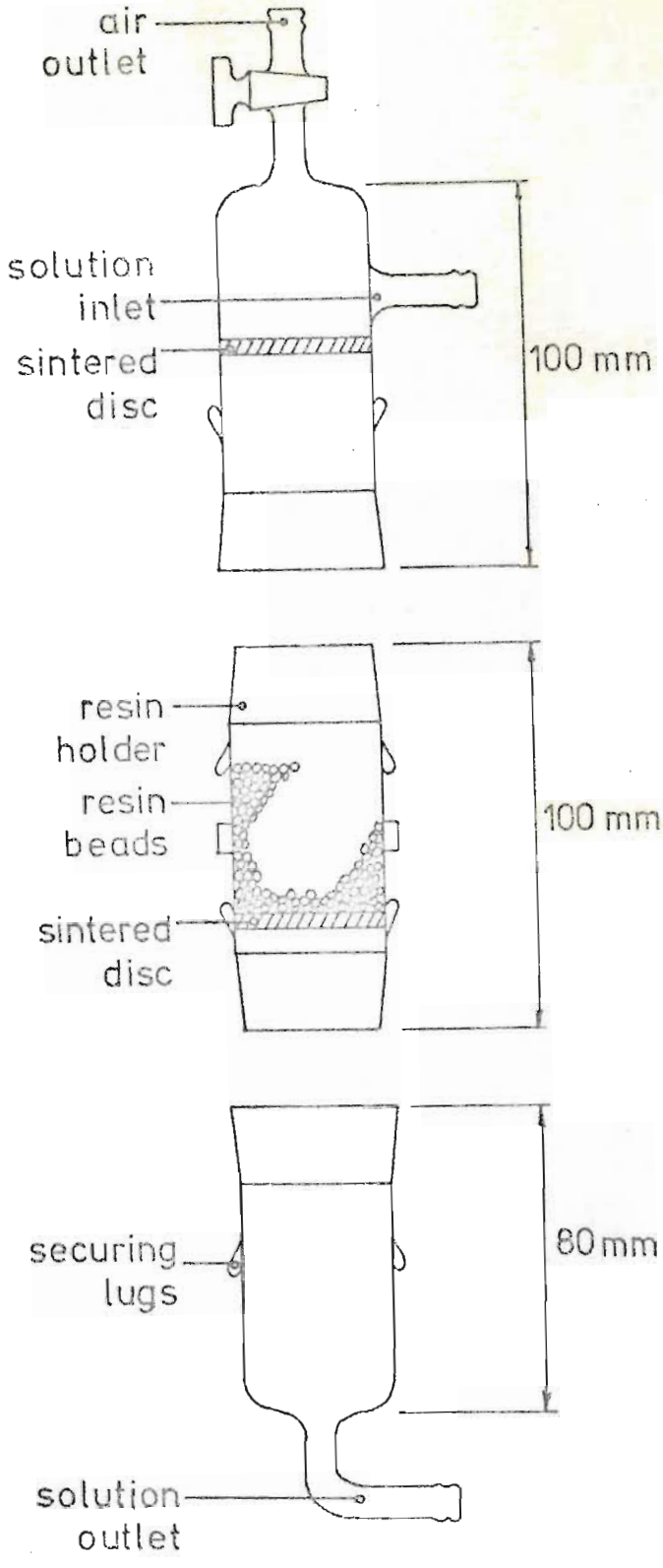
PERRY (1963) gives an expression for the centrifugal force calculated as a function of diameter and speed.

$$F_c = 0{,}0000142\ (RPM)^2 d$$

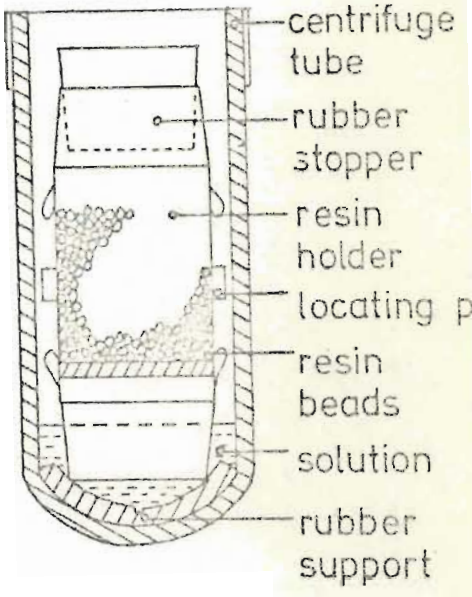
where d = diameter in inches

RPM = revolutions per minute

F_c = centrifugal force in multiples of gravity g.



(a)



(b)

Figure B.1a Cell for contacting ion exchange resin beads with solution.

Figure B.1b Resin holder in centrifuge tube.

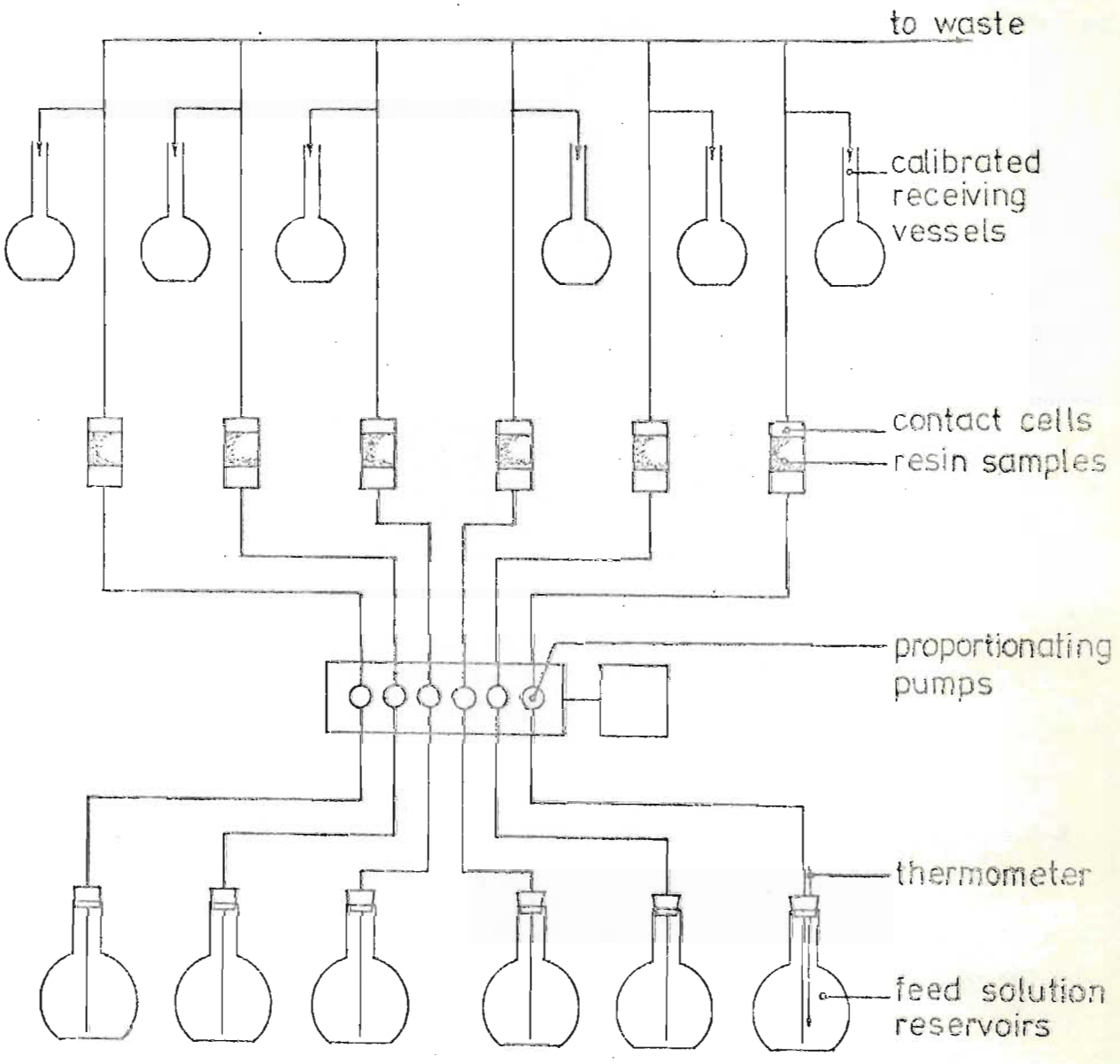


Figure B.2 Schematic diagram of multiple contacting apparatus.

For diameter of 17 cm at RPM of 2400 the centrifugal force is 550 g. Centrifugation at these conditions for a ten minute period is adopted as the standard technique for this work as suggested by HELFFERICH (1962).

APPENDIX C

DETAILED DESCRIPTION OF PROCEDURE

C.1 Preparation of ion exchange resin

The ion exchange resin Amberlite 400 as supplied is washed with deionised water. Thereafter 1 M sodium sulphate is passed through the resin until no chloride is detected in the effluent.

The resin is stored in contact with 1 M sodium sulphate until required, when it is separated from the sulphate solution by centrifugation.

C.2 Charging of resin holders

The resin holders are washed, centrifuged and weighed. Ten millimetres of resin in the sulphate form measured as a free settled volume is transferred to each of the resin holders. The holders and resin samples are centrifuged for ten minutes at 2400 RPM and then weighed. This is the standard centrifugation procedure used.

This proved to be a reproducible method of measuring the quantity of resin in the resin holders.

The average mass of thirty 10 ml samples of free settled resin in the sulphate form is 6,8572 gm with a standard deviation of ± 0,0385 gm.

C.3 Temperature control

The experiments were performed in an air conditioned laboratory. Solution temperatures varied slightly, the average temperature recorded was 295 ± 3^{o}K. These variations are not significant for the systems

discussed in this work (HELFFERICH, 1962 and YANO and KATAOKA, 1960). All calculations involving temperature dependent variables are completed using data at 298^{O}K.

C.4 Equilibrium period

It is essential that the time of contact of the resin with the solution should be long enough for attainment of equilibrium. HELFFERICH (1962) states that for strong base resins of the usual bead size (0,42 - 0,15 mm) and moderate crosslinking (4 to 10% DVB), about 30 minutes is ample. This value probably applies to simple ions and not complexes which are encountered in this work.

From the workof BARNES *et al* (1974), concerning the kinetics of anion exchange of uranium from aqueous sulphuric acid solutions a period of 48 hours is sufficient for the slowest reaction in the systems discussed in this work.

STEIN (1962) in his study of the ionic equilibria and ion exchange of uranyl sulphate solutions used approximately three grams of resin and passed 4 litres of loading solution over a period of twenty four to forty eight hours.

C.5 Loading cycle

The equilibrium solution is passed through the contact cell until equilibrium between the resin and solution is achieved. In all cases 5 litres of solution is passed at an approximately constant flowrate of 100 ml/hr over 48 hours.

At equilibrium the resin holder is removed, sealed, ensuring solvent above the resin level in the holder and centrifuged at the standard conditions.

C.6 Wash cycle

All components and vessels are thoroughly washed with deionised water. In all cases two litres of deionised water is passed through the connection tubing overnight.

C.7 Elution cycle

Excess wash water is removed from the system with nitrogen gas. The resin holder is returned to the cell. The appropriate elution solution is passed through the cell, in all cases 2 litres of solution over 24 hours and collected in 2 litre volumetric flasks. These solutions are analysed for the concentration of resin species.

C.8 Capacity determinations

The capacity of the resin samples may be determined prior to the test equilibriation. The procedure differs slightly from that described in Appendix C.5 in that 2 litres of 0,9 M NaCl, 0,1 M HCl is used as the loading solution passed through the cell over 24 hours and the elution solution is 1 litre of 1 M KNO_3 passed through the cell over 24 hours.

The analysis of this 1 litre sample for chloride provides the capacity.

Capacity measurements have been performed on 103 samples. The average capacity obtained is 1,4073 equivalents/litre of free settled resin in sulphate form with a standard deviation of ± 0,0092. This agrees with the value of 1,4 equivalents/litre of wet resin reported by the manufacturers of the ion exchange resin.

APPENDIX D

CHEMICALS USED IN THE EQUILIBRIUM TESTS

D.1 Ion exchange resin

A strong base anionic polystyrene ion exchange resin, Amberlite 400 manufactured by Rohm & Haas Co. is used as supplied. The manufacturers specification is as follows:

Amberlite IRA - 400 Styrene 8% DVB

Chloride form

Effective size 0,38 - 0,45 mm

Moisture content 42 - 48%

Total exchange capacity 1,4 equivalents/litre of wet resin.

D.2 Loading solutions

Chemically pure reagents are used in the preparation of the solutions to be equilibriated with the resin. The solvent is distilled water.

D.3 Elution solution

Analytical grade reagents are used in the preparation of the elution solutions since the concentrations of the eluants are high compared to the species eluted from the resin. The solvent is distilled water.

APPENDIX E

METHODS OF ANALYSIS

E.1 Uranium

Principle

A polorographic method for the determination of uranium has been described by LEGGE (1957). The wave corresponding to the reduction of uranium as the uranyl ion from +6 to +5 state is used for the analysis. The method of standard addition is applied and polarograms are recorded from 0 to -0,5 V. Reduction reaction is:

$$UO_2^{++} + e^- = UO_2^+$$

Application

The method of standard addition increases the field of application for this technique. It is applicable to the uranium bearing eluates of 1M KNO_3, 1M NaCl and 0,1 M $NaClO_4$.

Apparatus

Electrode assembly, Radiometer type E65. Drop life timer, Radiometer type DLT1. Polariter, Radiometer type PO4G.

Reagents

Electrolyte: Dissolve 2 g of ascorbic acid in 50 ml of distilled water, add 10 ml of 0,5 N H_2SO_4 and dilute to 100 ml distilled water.

Standard uranium: 0,05 M, dissolve pure dry U_3O_8 in nitric acid, add sulphuric acid, fume and make up to 1 litre with distilled water.

Procedure

Pipette 10 ml aliquot of sample into the polarograph measuring cell. Add 10 ml of the ascorbic acid electrolyte to the sample. Deaerate sample for ten minutes with water saturated nitrogen gas. Set the drop life timer to 1 second. Adjust the mercury reservoir to give a head of 50 cm. Record the polarogram from zero potential to -0,5 volts.

From the wave height estimate the volume of standard uranium solution which when added to the sample will produce a wave approximately twice that of the sample.

Deaerate for a few minutes. Record the polarogram from zero to -0,5 volts. Rinse the electrodes with distilled water. A typical set of polarograms is illustrated in Figure E.1.

Calculation

The wave height is measured according to the point method (WILLARD *et al*, 1965). The procedure is illustrated in Figure E.2. Construct in order of the alphabetical sequence the various lines. At the half wave potential L, the wave height JJ´ is estimated.

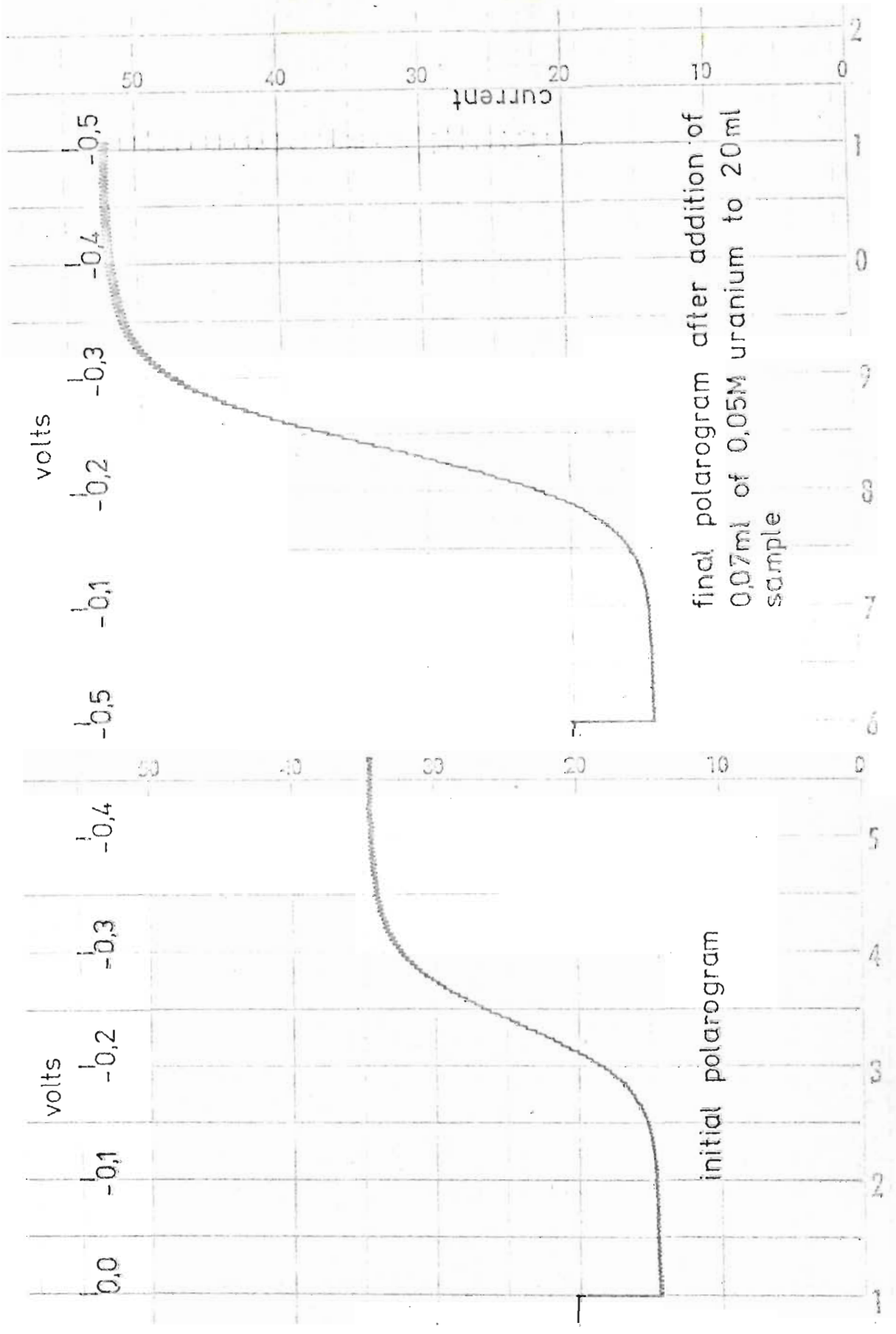


Figure E.1 Typical set of polarograms obtained in the known addition method for uranium analysis.

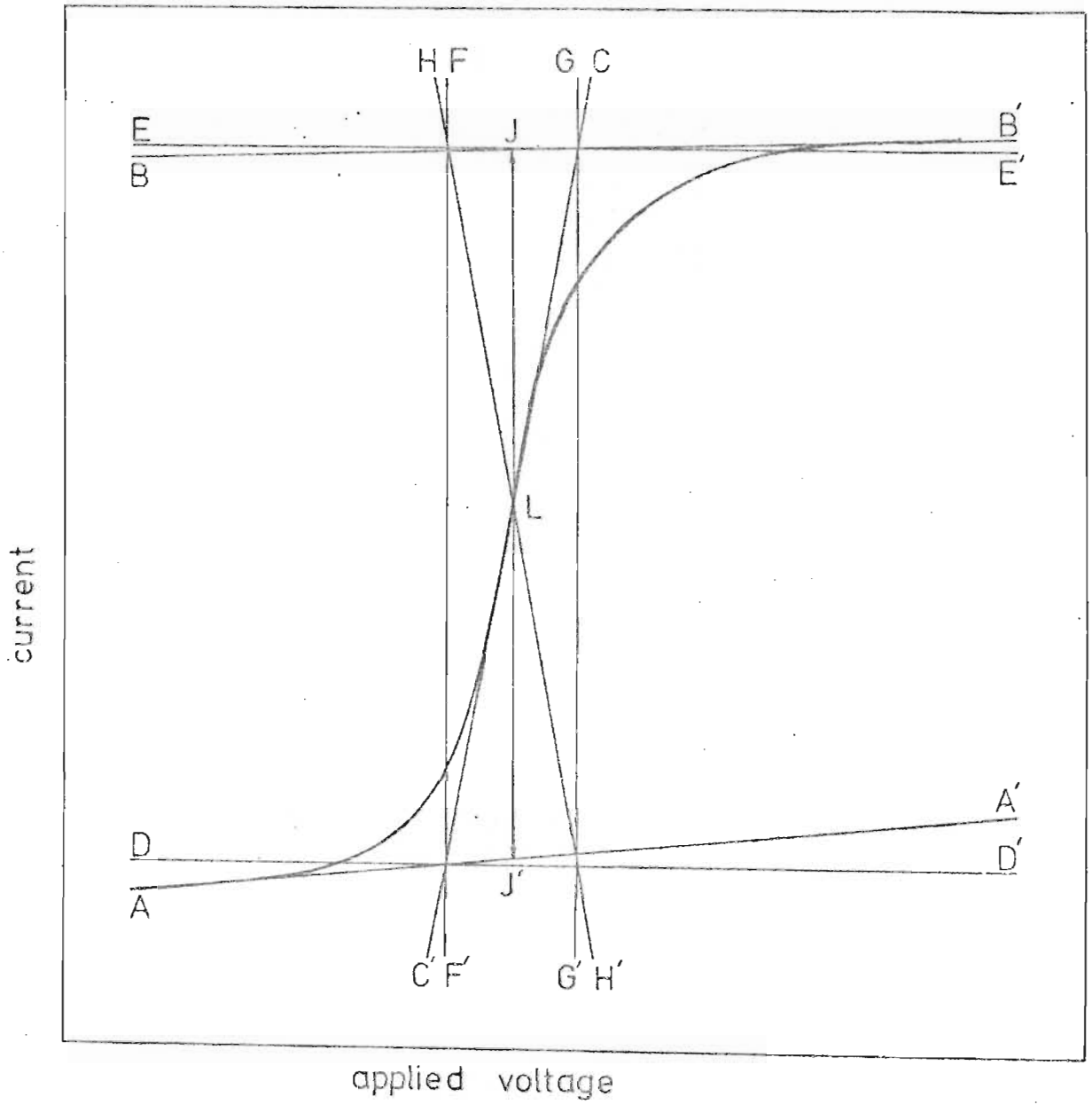


Figure E.2 Wave height measurement of polarogram according to the point method. Construction is performed in alphabetical sequence.

For the unknown solution

$$i_d = K C_x = h$$

where i_d is the measured current

K is a proportionality constant

C_x is the unknown concentration

h is the initial wave height.

After the addition of v ml of the standard solution with a concentration of C_s to V ml of unknown,

$$K C_x \left(\frac{V}{V + v}\right) + K C_s \left(\frac{V}{V + v}\right) = H$$

Rearranging for the unknown concentration C_x

$$C_x = \frac{v C_s h}{H(V + v) - h V}$$

For maximum precision the amount of standard added should be sufficient to double the original wave height.

E.2 Sulphate

Principle

The sulphate ions are precipitated as barium sulphate which is filtered dried and weighed. The method is outlined in Laboratory Method No. 16/2 (1966) with modifications for reducing the effect of

interfering ions as described by VOGEL (1961).

Nitrates are eliminated from the sample by evaporation with hydrochloric acid. Ascorbic acid is added to complex the uranium and prevent co-precipitation.

Application

The method is applicable to elution solutions of 1M sodium chloride, 0,1 M sodium perchlorate and 0,1 M sodium carbonate containing chloride, nitrate, uranyl and sodium ions and sulphuric acid.

Apparatus

Sintered glass crucibles, porosity No. 4.

Reagents

Barium chloride solution, 5%

Dissolve 50 g of barium chloride (A.R. grade) in 1 litre of distilled water.

Hydrochloric acid wash solution, 0,2%

Add 2 ml of hydrochloric acid to 1 litre of distilled water.

Ascorbic acid, 5%

Dissolve 50 g of ascorbic acid (A.R. grade) in 1 litre of distilled water. Filter solution if not clear.

Hydrochloric acid

(A.R. grade).

Procedure

Pipette the appropriate amount of the sample into a 500 ml beaker.

Evaporate to dryness on a water-bath.

Add 10 ml of hydrochloric acid and again evaporate to dryness on the water-bath.

Add 2 ml of hydrochloric acid and 50 ml of water, heat until the salts are in solution.

Dilute to 300 ml with distilled water, heat to boiling, add 20 mls of 5% ascorbic acid and add slowly 35 ml of hot barium chloride solution.

Keep the solution at about 80°C on a water-bath for one hour and then set aside to cool to room temperature.

Filter the solution through a No. 4 sintered glass crucible and wash the precipitate five times with hydrochloric wash solution and five times with cold distilled water.

Place in oven at 110°C for half an hour. Cool in dessicator for fifteen minutes and weigh the crucible.

Duplicate blank determinations are made with the pure elution solutions.

Calculation

For M_s = weight (grams) of $BaSO_4$ for sample determination

M_b = weight (grams) of $BaSO_4$ for blank determination

$$SO_4 \text{ concentration (g/l)} = \frac{(M_s - M_b) \times 411,5}{\text{Volume of sample (millilitres)}}$$

E.3 Chloride

Principle

The potentiometric titration of the chloride ion with a solution of silver nitrate as titrant is presented by PETERSEN (1966).

A clean silver electrode and mercurous sulphate reference electrode are used to record the potential difference with added volume of titrant to produce a titration curve. The equivalence point i.e. when all the chloride ions are titrated is the inflection point on the curve. This corresponds to a potential difference at which the activities of the silver and chloride ions are identical. This potential may be calculated from

$$E = K + \frac{RT}{F} \ln a_{Ag^+}$$

where E is the potential difference

K is a constant

R is the gas constant

F is the Faraday

a_{Ag+} is the activity of the silver ion in the solution.

However the activity depends on the composition of solution, thus the end point is determined experimentally. In practice the titration is best accomplished in a solution of sulphuric acid, approximately 1,5 N H_2SO_4.

Application

The method is applicable to elution solutions of 1M potassium nitrate, 0,1 M sodium perchlorate and 0,1 M sodium carbonate containing sulphate, uranyl, nitrate and sodium or potassium ions.

Apparatus

Electrode combination

Silver electrode, Radiometer type P4011.

Mercurous sulphate reference electrode, Radiometer type K601.

Titration equipment

Automatic titrator, Radiometer type TTT2.

Servograph, Radiometer type REC51 with pH meter Interface unit type REA100.

Titration assembly, Radiometer type TTA3.

Autoburette, Radiometer type ABU13.

Reagents

Standard silver nitrate 0,02 N.

Concentrated sulphuric acid A.R. grade.

Standard sodium chloride 0,02 N in 1 M KNO_3.

Procedure

A manual titration is performed to determine the end point of the titration for the particular standard chloride solution.

Pipette 20 ml of the standard sodium chloride solution into a titration vessel. Add 1 ml of concentrated sulphuric acid. Stir well and allow to cool. Titrate with standard silver nitrate beyond the end point. A typical titration curve is illustrated in Figure E.3. Determine the end-point as the point of inflection on this curve.

Set the end point of the titrator. Pipette an aliquot of the sample into the titration vessel and titrate automatically to the preset point.

Calculation

$$\text{Chloride concentration } (Cl^-) = \frac{v_s \times 0{,}02}{V} \text{ (equivalents/l)}$$

where v_s = volume in millimetres of silver nitrate

V = volume in millimetres of sample.

E.4 Acid

Principle

The hydrogen ion is titrated automatically with a standard solution of sodium hydroxide to be predetermined end point.

Application

The method is applicable to the elution solutions 1M KNO_3, 1M NaCl and 0,1 M $NaClO_4$, for the estimation of the bisulphate concentration in the resin phase provided no uranyl ions are present.

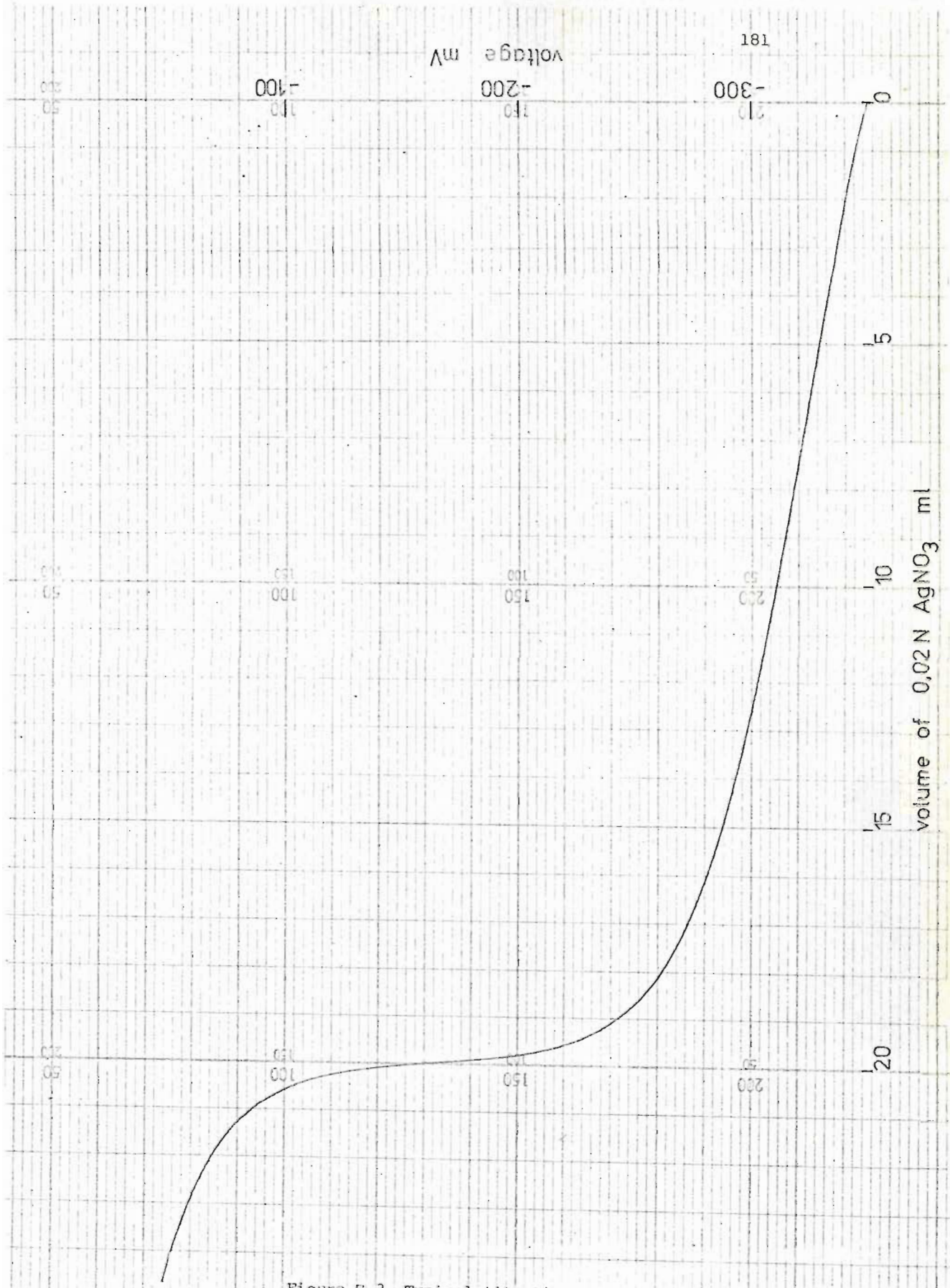


Figure E.3 Typical titration curve of the chloride ion with silver nitrate.

Apparatus

Combination pH electrode, Radiometer type GK2301B,
Titration equipment used for the chloride analysis.

Reagents

Standard sodium hydroxide 0,1 N.

Procedure

Pipette a suitable aliquot into the titration vessel. Titrate automatically with sodium hydroxide to the set point. A blank is determined similarly.

Calculation

$$\text{Hydrogen ion concentration (H)} = \frac{(v_s - v_b)\ (0{,}02)}{V} \text{ (equivalents l)}$$

where v_s = volume in millilitres of sodium hydroxide required for sample.

v_b = volume in millilitres of sodium hydroxide required for blank determination.

V = volume in millilitres of sample.

E.5 Nitrate

Principle

A UV spectrophotometric method for the determination of nitrate ion in the range 0 - 11 mg/l NO_3 - N is described in Standard Methods (1971).

Absorbance by nitrate in dilute acid at wavelength of 220 nm follows Beer's law up to 11 mg/l NO_3 - N.

Application

Solutions without dissolved organic matter or turbidity are suitable. The method is applicable to solutions containing chloride.

The elution solutions 1 M NaCl, 0,1 M $NaClO_4$ have been analysed for nitrate. Uranium interferes with the analysis.

Apparatus

UV Spectrophotometer, Unicam SP1700
Recorder, Unicam AR25
Automatic sample changer, Unicam SP40 AU
Flow through cell, 10 mm UV grade silica.

Procedure

Prepare a set of standard nitrate solutions in the range 0 - 11 mg/l NO_3 - N such that the concentration of the eluting ions chloride and perchlorate, are the same as in the diluted unknown sample.

Dilute the unknown samples such that the nitrate concentration is less than 11 mg/l NO_3 - N.

Introduce the standard solutions and the unknown samples into the sample holders on the automatic sample changer.

Set the wavelength at 220 nm and read the absorbance of the samples passing through the flow cell.

If uranium is present in the samples a standard absorbance curve is prepared. The absorbance due to the known amount of uranium in the sample is subtracted from the absorbance of the sample.

APPENDIX F

TABULATED EXPERIMENTAL AND PREDICTED DATA

Wilson Parameters			Equilibrium Constant
Λ_{ij}	Cl	NO_3	
Cl	1,0	2,4627	$K_{Cl}^{NO_3} = 3,780$
NO_3	0,39121	1,0	

Solution Normality	$x^*_{NO_3}$	λ_{EXP}	$\gamma^{NO_3}_{FIT}$	γ^{Cl}_{FIT}	λ_{FIT}
0,2 N	0,206	5,04	0,786	0,971	4,67
	0,311	4,17	0,854	0,944	4,18
	0,473	3,68	0,926	0,896	3,66
	0,588	3,41	0,959	0,861	3,39
	0,756	3,18	0,988	0,812	3,11
	0,871	3,10	0,997	0,780	2,96
0,4 N	0,194	4,74	0,777	0,974	4,74
	0,297	3,97	0,846	0,947	4,23
	0,461	3,57	0,922	0,900	3,69
	0,578	3,34	0,957	0,864	3,41
	0,749	3,12	0,987	0,814	3,12
	0,867	2,93	0,997	0,781	2,96

Table F.1 Comparison of experimental and fitted equilibrium quotients using the Wilson parameters and equilibrium constant quoted for the binary system Amberlite 400, 0,2 and 0,4 N mixture of $NaNO_3$ and NaCl at 298°K. Fitted values of the activity coefficients at 298°K. This data is presented graphically in Figures 4.1 and 4.4.

Wilson Parameters			Equilibrium Constant
Λ_{ij}	SO_4	Cl	
SO_4	1,0	0,21192	$K^{*Cl}_{SO_4} = 5,104$
Cl	3,7355	1,0	

Solution Normality	x_{Cl}	λ_{EXP}	γ^{Cl}_{FIT}	$\gamma^{SO_4}_{FIT}$	λ_{FIT}
0,2 N	0,279	10,81	0,685	0,974	10,60
	0,447	7,99	0,756	0,920	8,22
	0,657	5,25	0,860	0,780	5,39
	0,792	3,72	0,930	0,631	3,72
	0,891	2,51	0,975	0,488	2,62
0,4 N	0,378	9,27	0,725	0,947	9,19
	0,566	6,60	0,813	0,853	6,60
	0,764	4,15	0,916	0,666	4,05
	0,873	2,95	0,968	0,516	2,81

Table F.2 Comparison of experimental and fitted equilibrium quotients using the Wilson parameters and equilibrium constant quoted for the binary system Amberlite 400, 0,2 and 0,4N mixture of Na_2SO_4, and NaCl at 298°K. Fitted values of the activity coefficients at 298°K. This data is presented graphically in Figures 4.2 and 4.5.

Wilson Parameters			Equilibrium Constant
Λ_{ij}	SO_4	NO_3	
SO_4	1,0	0,65419	$K_{SO_4}^{NO_3} = 72,939$
NO_3	3,1159	1,0	

Solution Normality	$x_{NO_3}^*$	λ_{EXP}	$\gamma_{FIT}^{NO_3}$	$\gamma_{FIT}^{SO_4}$	λ_{FIT}
0,2 N	0,599	94,68	0,764	0,753	94,16
	0,741	49,83	0,866	0,581	56,41
	0,881	28,81	0,961	0,367	28,99
	0,941	19,40	0,989	0,273	20,36
	0,979	16,56	0,998	0,215	15,71
	0,989	13,42	0,999	0,199	14,54
0,4 N	0,695	70,57	0,833	0,642	67,43
	0,823	37,76	0,925	0,459	39,13
	0,929	22,14	0,984	0,292	21,97
	0,971	17,43	0,997	0,227	16,62
0,6 N	0,753	60,49	0,875	0,563	53,59
	0,867	32,81	0,952	0,389	31,35
	0,951	19,74	0,992	0,257	19,07
	0,981	15,67	0,998	0,212	15,51
	0,994	14,10	1,000	0,193	14,07

Table F.3 Comparison of experimental and fitted equilibrium quotients using the Wilson parameters and equilibrium constant quoted for the binary system Amberlite 400, 0,2, 0,4 and 0,6 N, mixture of Na_2SO_4 and $NaNO_3$ at 298°K. Fitted values of the activity coefficients at 298°K. This data is presented graphically in Figures 4.3 and 4.6.

Wilson Parameters			Equilibrium Constant
Λ_{ij}	SO_4	Cl	
SO_4	1,0	0,21192	$K^{Cl}_{SO_4} = 5,104$
Cl	3,7355	1,0	

Solution Normality	SO_4 - Cl					
	Solution		Resin Phase (Mole /ℓ Resin)			
	Equivalent Fraction		Experimental		Fitted	
N	ΣSO_4	Cl	SO_4^*	Cl	SO_4	Cl
0,2	0,90	0,10	0,5880	0,2880	0,5873	0,2255
	0,80	0,20	0,5002	0,4036	0,4967	0,4066
	0,60	0,40	0,3585	0,6880	0,3548	0,6904
	0,40	0,60	0,2416	0,9208	0,2408	0,9183
	0 20	0,80	0,1383	1,1264	0,1349	1,1302
	0 10	0,90	0,0892	1,2256	0,0766	1,2468
0,4	0,90	0,10	0,5386	0,3268	0,5303	0,3394
	0,80	0,20	0,4252	0,5536	0,4180	0,5640
	0,60	0,40	0,2679	0,8692		
	0,40	0,60	0,1584	1,0872	0,1695	1,0611
	0,20	0,80	0,0851	1,2328	0,0872	1,2256
	0,10	0,90	0,0560	1,2920	0,0467	1,3067

Table F.4 Comparison of experimental and fitted concentration of resin species for binary system Amberlite 400, 0,2 and 0,4 N mixture of Na_2SO_4 and NaCl at 298°K. Capacity assumed as 1,4 equiv/ℓ resin. Wilson parameters and equilibrium constant are reported. This data is presented graphically in Figure 4.7.

Wilson Parameters			Equilibrium Constant
Λ_{ij}	Cl	NO_3	
Cl	1,0	2,4627	$K_{Cl}^{NO_3} = 3,780$
NO_3	0,39121	1,0	

Solution Normality	Cl - NO_3					
	Solution		Resin Phase (Mole /ℓ Resin)			
	Equivalent Fraction		Experimental		Fitted	
N	Cl	NO_3	Cl	NO_3^*	Cl	NO_3
0,2	0,95	0,05	1,1152	0,2888	1,1264	0,2736
	0,90	0,10	0,9672	0,4368	0,9637	0,4363
	0,80	0,20	0,7404	0,6646	0,7396	0,6604
	0,70	0,30	0,5784	0,8256	0,5784	0,8216
	0,50	0,50	0,3416	1,0614	0,3466	1,0534
	0,30	0,70	0,1808	1,2232	0,1875	1,2125
0,4	0,95	0,05	1,1328	0,2712	1,1295	0,2705
	0,90	0,10	0,9864	0,4176	0,9679	0,4321
	0,80	0,20	0,7568	0,6482	0,7445	0,6555
	0,70	0,30	0,5920	0,8120	0,5834	0,8167
	0,50	0,50	0,3516	1,0514	0,3507	1,0493
	0,30	0,70	0,1860	1,2180	0,1835	1,2166

Table F.5 Comparison of experimetnal and fitted concentration of resin species for binary system Amberlite 400, 0,2 and 0,4 N mixture of $NaNO_3$ NaCl at 298°K. Capacity assumed as 1,4 equiv/ℓ resin. Wilson parameters and equilibrium constant are reported. This data is presented graphically in Figure 4.8.

	Wilson Parameters		Equilibrium Constant
Λ_{ij}	SO_4	NO_3	$K_{SO_4}^{NO_3} = 72,939$
SO_4	1,0	0,65419	
NO_3	3,1159	1,0	

Solution Normality N	SO_4 - NO_3					
	Solution Equivalent Fraction		Resin Phase (Mole/ℓ Resin)			
			Experimental		Fitted	
	SO_4	NO_3	SO_4	NO_3*	SO_4	NO_3
0,2	0,90	0,10	0,4044	0,6039	0,4012	0,5976
	0,80	0,20	0,2896	0,8288	0,2777	0,8446
	0,60	0,40	0,1491	1,1088	0,1479	1,1041
	0,40	0,60	0,0788	1,2524	0,0760	1,2481
	0,20	0,80	0,0291	1,3537	0,0302	1,3397
	0,10	0,90	0,0146	1,3749	0,0135	1,3730
0,4	0,90	0,10	0,3243	0,7405	0,3306	0,7388
	0,80	0,20	0,2112	0,9846	0,2074	0,9853
	0,60	0,40	0,0938	1,2224	0,0936	1,2129
	0,40	0,60	0,0398	1,3313	0,0410	1,3180
0,6	0,90	0,10	0,2767	0,8456	0,2869	0,8261
	0,80	0,20	0,1654	1,0783	0,1676	1,0648
	0,60	0,40	0,0660	1,2741	0,0672	1,2656
	0,40	0,60	0,0266	1,3499	0,0267	1,3465
	0,20	0,80	0,0086	1,3939	0,0085	1,3830

Table F.6 Comparison of experimental and fitted concentration of resin species for binary system Amberlite 400, Na_2SO_4, $NaNO_3$ at 298°K. Capacity assumed as 1,4 equiv./l resin. Wilson parameters and equilibrium constant used are reported. This data is graphically presented in Figure 4.9.

Wilson parameters			Equilibrium constant
Λ_{ij}	SO_4	HSO_4	
SO_4	1,0	0,9846	$K_{SO_4}^{HSO_4} = 5,098$
HSO_4	2,8124	1,0	

SO_4 - HSO_4						
Mole/ℓ Resin		Mole Fraction	Equilibrium Quotient		Resin Phase Activity Coefficient	
SO_4*	HSO_4	HSO_4	λ_{Exp}	λ_{Fit}	$\gamma_{fit}^{SO_4}$	$\gamma_{Fit}^{HSO_4}$
0,520	0,370	0,4157	11,69	12,01	0,8612	0,6046
0,522	0,374	0,4174	11,82	11,94	0,8599	0,6059
0,521	0,374	0,4179	11,85	11,92	0,8596	0,6062
0,350	0,688	0,6628	4,43	4,89	0,6142	0,7995
0,349	0,704	0,6686	4,59	4,78	0,6070	0,8043
0,357	0,696	0,6610	4,38	4,94	0,6164	0,7980
0,2840	0,8260	0,7441	3,62	3,46	0,5081	0,8657
0,3127	0,7376	0,7023	4,47	4,15	0,5638	0,8319
0,3461	0,6968	0,6681	5,13	4,79	0,6076	0,8039
0,3774	0,6412	0,6295	6,09	5,60	0,6547	0,7721
0,4105	0,5740	0,5830	7,60	6,70	0,7078	0,7340
0,4658	0,4564	0,4949	8,61	9,21	0,7961	0,6640
0,2040	0,9630	0,8252	2,31	2,35	0,3958	0,9266
0,2593	0,8625	0,7689	3,16	3,09	0,4742	0,8851
0,5707	0,2396	0,2957	18,58	17,44	0,9340	0,5224
0,5870	0,1870	0,2416	21,71	20,44	0,9573	0,4887
0,6085	0,1430	0,1903	24,24	23,64	0,9743	0,4584
0,6420	0,0870	0,1193	26,98	28,70	0,9903	0,4195

Figure F.7 Comparison of experimental and fitted equilibrium quotients using the Wilson parameter and equilibrium constant quoted for the binary system Amberlite 400, mixture of Na_2SO_4, and H_2SO_4 at 298°K. Fitted values of the activity coefficients at 298°K. This data is graphically presented in Figure 5.1 and 5.2

Wilson Parameters			Equilibrium Constant
Λ_{ij}	$SO_4^=$	HSO_4^-	$K_{SO_4}^{HSO_4} = 5,098$
$SO_4^=$	1,0	0,9846	
HSO_4^-	2,8124	1,0	

$SO_4^= - HSO_4^-$						
Solution Phase (M)			Resin Phase (Mole/ℓ Resin)			
$\Sigma SO_4^=$	H^+	Na^+	SO_4^* exp	HSO_4^- exp	$SO_4^=$ fit	HSO_4^- fit
0,3641	0,0593	0,6689	0,520	0,370	0,5148	0,3705
0,3641	0,0593	0,6689	0,522	0,374	0,5148	0,3705
0,3641	0,0593	0,6689	0,521	0,374	0,5148	0,3705
0,3619	0,1866	0,5373	0,350	0,688	0,3452	0,7096
0,3619	0,1866	0,5373	0,349	0,704	0,3452	0,7096
0,3619	0,1866	0,5373	0,357	0,696	0,3452	0,7096
0,4988	0,2775	0,7201	0,2840	0,826	0,2889	0,8222
0,4706	0,2213	0,7200	0,3127	0,7376	0,3269	0,7461
0,4538	0,1875	0,7201	0,3461	0,6968	0,3542	0,6916
0,4373	0,1547	0,7200	0,3774	0,6412	0,3849	0,6303
0,4209	0,1219	0,7200	0,4105	0,5740	0,4211	0,5577
0,4045	0,0891	0,7200	0,4658	0,4564	0,4655	0,4691
0,4638	0,4180	0,5000	0,2040	0,9630	0,2092	0,9817
0,3981	0,2978	0,5000	0,2593	0,8625	0,2647	0,8706
0,2650	0,0290	0,5000	0,5707	0,2396	0,5812	0,2375
0,2613	0,0212	0,5000	0,5870	0,1870	0,6060	0,1880
0,2575	0,0153	0,5000	0,6085	0,1430	0,6271	0,1457
0,2538	0,0087	0,5000	0,6420	0,0870	0,6544	0,0912

Table F.8 Comparison of experimental and fitted concentration of resin species for binary system Amberlite 400, mixture of Na_2SO_4 and H_2SO_4 at 298°K. Capacity assumed is 1,4 equiv./l resin. Wilson parameters and equilibrium constant are reported. This data is graphically presented inFigure 5.4.

Wilson Parameters				Equilibrium Constant
Λ_{ij}	SO_4	HSO_4	Cl	
SO_4	1,0	0,9846	0,21192	$K_{SO_4}^{HSO_4} = 5,098$
HSO_4	2,8124	1,0	0,74146	
Cl	3,7355	1,2865	1,0	$K_{SO_4}^{*Cl} = 5,104$

Resin Phase				Equilibrium Quotients			
Mole/ℓ R	Mole Fraction			Experimental		Fitted	
SO_4^*	SO_4^*	HSO_4	Cl	$\lambda_{SO_4}^{HSO_4}$	$\lambda_{SO_4}^{Cl}$	$\lambda_{SO_4}^{HSO_4}$	$\lambda_{SO_4}^{Cl}$
0,2566	0,2244	0,6821	0,0935	3,014	2,937	3,131	2,765
0,2397	0,2066	0,6205	0,1729	2,853	2,528	2,993	2,630
0,2048	0,1714	0,5020	0,3266	2,711	2,299	2,726	2,372
0,1670	0,1354	0,3893	0,4753	2,391	2,242	2,450	2,121
0,1245	0,0976	0,3042	0,5982	2,439	2,174	2,105	1,846
0,1152	0,0896	0,2304	0,6800	2,265	2,004	2,166	1,867
0,4722	0,5089	0,2975	0,1937	11,471	6,901	11,239	6,825
0,4270	0,4388	0,2199	0,3413	8,017	5,566	10,184	6,057
0,3149	0,2902	0,1419	0,5579	6,067	4,311	6,929	4,309
0,2237	0,1902	0,0816	0,7282	4,705	3,480	4,971	3,267
0,1311	0,1033	0,0394	0,8573	3,666	2,829	3,295	2,423
0,0945	0,0724	0,0199	0,9077	2,581	2,164	2,773	2,168

Table F.9 Comparison of experimental and fitted equilibrium quotients using the Wilson parameters and equilibrium constants quoted for the ternary system Amberlite 400, mixture of Na_2SO_4, NaCl and H_2SO_4 at 298°K. This data is graphically presented in Figures 5.5 and 5.6.

Wilson Parameters				Equilibrium Constant
Λ_{ij}	SO_4	HSO_4	Cl	
SO_4	1,0	0,9846	0,21192	$K_{SO_4}^{HSO_4} = 5,098$
HSO_4	2,8124	1,0	0,74146	
Cl	3,7355	1,2865	1,0	$K_{SO_4}^{*Cl} = 5,104$

SO_4 - HSO_4 - Cl					
Resin Phase (Mole/ℓ Resin)					
Experimental			Fitted		
SO_4*	HSO_4	Cl	SO_4	HSO_4	Cl
0,2566	0,780	0,1069	0,2546	0,7878	0,1030
0,2397	0,720	0,2006	0,2361	0,7261	0,2018
0,2048	0,600	0,3904	0,2035	0,5985	0,3945
0,1670	0,480	0,5861	0,1687	0,4888	0,5738
0,1245	0,388	0,7630	0,1348	0,3846	0,7458
0,1152	0,296	0,8736	0,1192	0,2974	0,8642
0,4722	0,276	0,1797	0,4733	0,2742	0,1792
0,4270	0,214	0,3321	0,4519	0,2315	0,3367
0,3149	0,154	0,6163	0,3155	0,1638	0,6053
0,2237	0,096	0,8567	0,2285	0,1003	0,8428
0,1311	0,050	1,0878	0,1421	0,0563	1,0651
0,0945	0,026	1,1851	0,0944	0,0269	1,1843

Table F.10 Comparison of experimental and fitted resin phase equilibrium composition for solutions specified in Table 5.2 for ternary system Amberlite 400, mixture of Na_2SO_4, NaCl and H_2SO_4. Capacity assumed as 1,4 equiv./l resin. Wilson parameters and equilibrium constants reported. This data is presented graphically in Figure 5.7.

Wilson Parameters				Equilibrium Constant
Λ_{ij}	SO_4	HSO_4	NO_3	
SO_4	1,0	0,9846	0,65419	$K_{SO_4}^{HSO_4} = 5,098$
HSO_4	2,8124	1,0	2,6912	
NO_3	3,1159	0,27678	1,0	$K_{SO_4}^{NO_3} = 72,939$

Resin Phase					Equilibrium Quotients			
Mole /ℓ Resin		Mole Fraction			Experimental		Fitted	
SO_4^*	NO_3^*	SO_4^*	HSO_4	NO_3^*	$\lambda_{SO_4}^{HSO_4}$	$\lambda_{SO_4}^{NO_3}$	$\lambda_{SO_4}^{HSO_4}$	$\lambda_{SO_4}^{NO_3}$
0,1972	0,3433	0,1642	0,5499	0,2859	2,678	40,39	2,866	45,34
0,1585	0,5250	0,1285	0,4459	0,4256	2,352	26,48	2,579	32,67
0,0986	0,8127	0,0756	0,3014	0,6230	2,187	20,40	2,081	21,41
0,0557	1,0032	0,0415	0,2117	0,7468	2,224	19,44	1,758	16,71
0,0361	1,1266	0,0265	0,1475	0,8260	2,096	16,42	1,672	15,19
0,0340	1,1754	0,0251	0,1088	0,8662	1,716	12,55	1,733	15,28
0,3344	0,5188	0,3144	0,1978	0,4878	7,659	75,11	7,718	72,97
0,2528	0,7550	0,2190	0,1268	0,6541	5,253	43,44	5,669	47,77
0,1374	1,0464	0,1085	0,0654	0,8262	3,293	26,78	3,351	26,96
0,0734	1,2152	0,0551	0,0330	0,9119	2,434	19,68	2,413	19,53
0,0306	1,3166	0,0224	0,0152	0,9624	2,097	17,56	1,906	15,72

Table F.11 Comparison of experimental and fitted equilibrium quotients using the Wilson Parameters and equilibrium constants quoted for the ternary system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$ and H_2SO_4 at 298°K. This data is presented graphically in Figures 5.8 and 5.9.

Wilson Parameters				Equilibrium Constants
Λ_{ij}	SO_4	HSO_4	NO_3	
SO_4	1,0	0,9846	0,65419	$K_{SO_4}^{HSO_4} = 5,098$
HSO_4	2,8124	1,0	2,6912	
NO_3	3,1159	0,27678	1,0	$K_{SO_4}^{NO_3} = 72,939$

SO_4 - HSO_4 - NO_3					
Resin Phase (Mole/ℓ Resin)					
Experimental			Fitted		
SO_4^*	HSO_4	NO_3^*	SO_4	HSO_4	NO_3
0,1972	0,6604	0,3433	0,1913	0,6647	0,3527
0,1585	0,5500	0,5250	0,1494	0,5493	0,5519
0,0986	0,3932	0,8127	0,0973	0,3815	0,8239
0,0557	0,2844	1,0032	0,0623	0,2737	1,0017
0,0361	0,2012	1,1266	0,0388	0,1888	1,1335
0,0340	0,1476	1,1754	0,0296	0,1378	1,2030
0,3344	0,2104	0,5188	0,3364	0,2123	0,5150
0,2528	0,1464	0,7550	0,2442	0,1469	0,7647
0,1374	0,0828	1,0464	0,1365	0,0830	1,0439
0,0734	0,0440	1,2152	0,0740	0,0440	1,2079
0,0306	0,0208	1,3166	0,0335	0,0209	1,3121
0,0124	0,0124	1,3578	0,0186	0,0116	1,3511

Table F.12 Comparison of experimental and fitted resin phase equilibrium composition for solutions specified in Table 5.3 for ternary system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$ and H_2SO_4. Capacity is 1,4 equiv./l resin. Wilson parameters and equilibrium constants are reported. This data is graphically presented in Figure 5.10.

Resin Phase								Experimental			Fitted		
Mole /ℓ Resin				Mole Fraction									
SO_4^*	HSO_4^*	$UO_2(SO_4)_3^*$	$UO_2(SO_4)_2^*$	SO_4^*	HSO_4^*	$UO_2(SO_4)_3^*$	$UO_2(SO_4)_2^*$	$\lambda_{SO_4}^{HSO_4}$	$\lambda_{SO_4}^{UO_2(SO_4)_3}$	$\lambda_{SO_4}^{UO_2(SO_4)_2}$	$\lambda_{SO_4}^{HSO_4}$	$\lambda_{SO_4}^{UO_2SO_4)_3}$	$\lambda_{SO_4}^{UO_2(SO_4)_2}$
0,3869	0,2808	0,07117	0,03822	0,4978	0,3613	0,09158	0,04931	10,356	4627,2	105,57	8,646	5038,5	98,93
0,3393	0,2464	0,09750	0,05250	0,4612	0,3349	0,13253	0,07136	9,593	3947,6	83,45	8,011	3737,3	66,36
0,2903	0,2109	0,12616	0,06794	0,4175	0,3033	0,18146	0,09771	8,682	3142,4	60,13	7,486	2843,4	45,98
0,2299	0,1672	0,14833	0,07987	0,3677	0,2674	0,23723	0,12774	7,643	3099,3	52,22	7,061	2238,3	33,32
0,2140	0,1559	0,16783	0,09037	0,3407	0,2482	0,26720	0,14387	7,078	2265,2	35,37	6,877	2012,0	28,87
0,1995	0,1454	0,17166	0,09244	0,3276	0,2388	0,28186	0,15177	6,804	2211,7	33,21	6,797	1918,4	27,08
0,3109	0,6389	0,03891	0,01848	0,3101	0,6372	0,03423	0,01843	4,451	4031,4	57,30	4,232	4394,9	53,99
0,2813	0,5782	0,05538	0,02982	0,2978	0,6121	0,05862	0,03156	4,274	3611,8	49,29	4,036	3492,2	42,81
0,2503	0,5148	0,08125	0,04375	0,2812	0,5784	0,09128	0,04915	4,036	3561,1	45,90	3,883	2737,8	33,51
0,2119	0,4365	0,10354	0,05576	0,2624	0,5404	0,12820	0,06903	3,764	2391,6	28,76	3,804	2213,8	27,04
0,1887	0,3891	0,12519	0,06741	0,2449	0,5051	0,16251	0,08751	3,512	2405,6	27,00	3,791	1897,1	23,11
0,1812	0,3741	0,13033	0,07018	0,2397	0,4950	0,17246	0,09286	3,437	1955,8	21,49	3,793	1824,1	22,20
0,1742	0,9831	0,02496	0,01344	0,1514	0,8152	0,02169	0,01168	2,144	3378,5	23,45	2,086	2229,3	18,92
0,1582	0,8491	0,04933	0,02657	0,1460	0,7839	0,04555	0,02453	2,066	2965,9	19,85	2,066	1892,7	16,77
0,1316	0,7078	0,08807	0,04743	0,1350	0,7260	0,09034	0,04864	1,911	2332,6	14,43	2,094	1507,9	14,25
0,2269	0,8568	0,01993	0,01073	0,2036	0,7689	0,01788	0,00963	2,729	2635,6	24,59	2,682	3072,7	28,79
0,2071	0,7806	0,04341	0,02337	0,1964	0,7403	0,04116	0,02217	2,632	2308,0	20,77	2,606	2520,3	24,36
0,1734	0,6534	0,08177	0,04403	0,1820	0,6859	0,08584	0,04622	2,439	1989,7	16,60	2,563	1899,8	19,26
0,1905	0,9284	0,02119	0,01141	0,1654	0,8063	0,01840	0,00991	2,288	2793,6	21,18	2,234	2473,8	21,42
0,1732	0,8428	0,04446	0,02394	0,1597	0,7772	0,04100	0,02208	2,209	2673,4	19,57	2,198	2086,9	18,79
0,1447	0,7033	0,08209	0,04421	0,1485	0,7219	0,08426	0,04537	2,053	2169,2	14,76	2,203	1639,5	15,68

Table F.13 Resin phase species distribtuion and comparison of experimental and fitted equilibrium quotients using the Wilson parameters and equilibrium constants quoted in Table 6.5, for system Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. This data is presented graphically in Figures 6.4, 6.5 and 6.6.

Resin Phase								Experimental			Fitted		
Mole/ℓ Resin				Mole Fraction									
SO_4^*	HSO_4^*	$UO_2(SO_4)_3^*$	$UO_2(SO_4)_3^*$	SO_4^*	HSO_4^*	$UO_2(SO_4)_3^*$	$UO_2(SO_4)_2^*$	$\lambda_{HSO_4 SO_4}$	$\lambda_{UO_2(SO_4)_3 SO_4}$	$\lambda_{UO_2(SO_4)_2 SO_4}$	$\lambda_{HSO_4 SO_4}$	$\lambda_{UO_2(SO_4)_3 SO_4}$	$\lambda_{UO_2(SO_4)_2 SO_4}$
0,2603	0,5875	0,05918	0,03187	0,2772	0,6258	0,06304	0,03394	3,894	3414,7	43,39	3,726	3141,4	37,04
0,2280	0,5137	0,08747	0,04710	0,2602	0,5862	0,09982	0,05375	3,657	2543,6	30,34	3,613	2446,5	29,02
0,1717	0,3844	0,13428	0,07231	0,2251	0,5040	0,17608	0,09481	3,168	1893,6	19,54	3,614	1729,8	20,65
0,2895	0,5842	0,04986	0,02685	0,3046	0,6147	0,05247	0,02825	4,392	3089,2	43,13	4,139	3736,4	46,21
0,2507	0,5036	0,07905	0,04256	0,2862	0,5750	0,09025	0,04860	4,131	2534,9	33,25	3,955	2799,4	34,56
0,1921	0,3859	0,12429	0,06693	0,2497	0,5017	0,16158	0,08701	3,604	1890,0	21,63	3,854	1929,8	23,67
0,3077	0,5616	0,04527	0,02437	0,3277	0,5981	0,04821	0,02596	4,857	3348,8	50,33	4,530	4199,9	54,55
0,2683	0,4898	0,07617	0,04101	0,3066	0,5596	0,08702	0,04686	4,543	2492,1	35,01	4,266	3050,3	39,11
0,2089	0,3818	0,11956	0,06438	0,2697	0,4929	0,15435	0,08311	3,995	1925,9	23,82	4,101	2091,3	26,34
0,3167	0,2438	0,10627	0,05723	0,4374	0,3367	0,14679	0,07904	8,893	3443,0	69,02	7,526	3339,6	56,36
0,2685	0,2061	0,13195	0,07105	0,3969	0,3031	0,19502	0,10501	8,093	2578,2	46,90	7,140	2615,8	40,82
0,1927	0,1472	0,17218	0,09272	0,3186	0,2434	0,28471	0,15331	6,496	1826,1	26,67	6,622	1873,7	26,17
0,3514	0,2516	0,08975	0,04832	0,4742	0,3395	0,12111	0,06521	9,917	3401,5	73,92	8,248	4055,9	74,32
0,2845	0,2034	0,12648	0,06810	0,4169	0,2980	0,18533	0,09979	8,725	2681,9	51,25	7,531	2808,8	45,34
0,2223	0,1582	0,15947	0,08587	0,3552	0,2528	0,25482	0,13721	7,447	1722,4	28,04	7,037	2115,1	30,93
0,3707	0,2440	0,08492	0,04573	0,4974	0,3273	0,11394	0,06135	10,743	3613,5	82,37	8,878	4424,6	85,58
0,3182	0,2092	0,11097	0,05976	0,4558	0,2997	0,15894	0,08559	9,849	2361,9	49,34	8,238	3326,8	57,88
0,2357.	0,1551	0,15313	0,08246	0,3762	0,2476	0,24447	0,13164	8,127	1748,1	30,14	7,419	2253,5	33,90

Table F.14 Resin phase specie distribution and comparison of experimental and fitted equilibrium quotients using the Wilson parameters and equilibrium constants as quoted in Table 6.5 for system Amberlite 400, mixtyre of Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. This data is presented graphically in Figures 6.4, 6.5 and 6.6.

Resin Phase								Experimental			Fitted		
Mole/ℓ Resin				Mole Fraction									
SO_4^*	HSO_4^*	$UO_2(SO_4)_3^*$	$UO_2(SO_4)_2^*$	SO_4^*	HSO_4^*	$UO_2(SO_4)_3^*$	$UO_2(SO_4)_2^*$	$\lambda_{SO_4}^{HSO_4}$	$\lambda_{SO_4}^{UO_2(SO_4)_3}$	$\lambda_{SO_4}^{UO_2(SO_4)_2}$	$\lambda_{SO_4}^{HSO_4}$	$\lambda_{SO_4}^{UO_2(SO_4)_3}$	$\lambda_{SO_4}^{UO_2(SO_4)_2}$
0,1132	0,4885	0,13810	0,07436	0,1391	0,6000	0,16961	0,09133	1,885	1839,6	11,73	2,525	1300,0	13,69
0,1063	0,3951	0,15709	0,08459	0,1431	0,5317	0,21139	0,11383	1,916	1842,9	12,08	2,845	1255,2	13,79
0,1394	0,2776	0,16689	0,08986	0,2070	0,4120	0,24770	0,13338	2,995	1512,5	14,35	3,990	1473,5	17,89
0,1102	0,1662	0,20272	0,10918	0,1874	0,2825	0,34457	0,18554	2,949	1789,6	15,37	4,780	1319,2	16,20
0,1511	0,1086	0,1980	0,10660	0,2677	0,1924	0,35088	0,18893	5,591	1490,1	18,29	6,527	1589,2	21,05
0,0952	0,3539	0,09934	0,23179	0,1220	0,4536	0,12731	0,29707	1,635	507,0	12,29	1,554	444,2	8,90
0,0959	0,4223	0,09106	0,21246	0,1168	0,5139	0,11081	0,25856	1,587	545,7	12,65	1,458	480,0	8,79
0,1037	0,1569	0,11954	0,27893	0,1574	0,2381	0,18136	0,42318	2,474	440,2	13,76	2,232	394,1	10,17
0,1298	0,2639	0,10250	0,23917	0,1765	0,3589	0,13940	0,32528	2,539	371,1	13,01	2,039	495,3	11,24
0,1433	0,1050	0,11607	0,27084	0,2256	0,1653	0,18274	0,42640	4,675	347,4	15,57	3,060	465,9	13,05

Table F.15 Resin phase speciesdistribution and comparison of experimental and fitted equilibrium quotients using the Wilson parameters and equilibrium constants quoted in Table 6.5 for the system Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. This data is graphically presented in Figures 6.4, 6.5 and 6.6.

Resin Phase			
Mole/ℓ Resin			
Experimental		Fitted	
ΣU	ΣSO_4	ΣU	ΣSO_4
0,1095	0,9707	0,1137	0,9426
0,1500	0,9783	0,1463	0,9614
0,1941	1,0118	0,1845	0,9842
0,2282	1,0041	0,2128	1,0016
0,2582	1,0709	0,2437	1,0212
0,2641	1,0709	0,2519	1,0264
0,0528	1,1296	0,0542	1,0598
0,0852	1,1279	0,0828	1,0650
0,1250	1,1525	0,1096	1,0696
0,1593	1,1094	0,1565	1,0808
0,1926	1,1198	0,1776	1,0869
0,2005	1,1142	0,19582	1,0924
0,0384	1,1805	0,0299	1,1975
0,0759	1,1617	0,0607	1,1981
0,1355	1,1720	0,1149	1,1944
0,0326	1,1634	0,0311	1,1895
0,0684	1,1685	0,0611	1,1759
0,1263	1,1685	0,1146	1,1829
0,0306	1,1600	0,0348	1,1536
0,0668	1,1823	0,0714	1,1516
0,1258	1,1874	0,1243	1,1524

Resin Phase			
Mole/ℓ Resin			
Experimental		Fitted	
ΣU	ΣSO_4	ΣU	ΣSO_4
0,0910	1,0743	0,0871	1,0788
0,1346	1,0914	0,1315	1,0865
0,2066	1,1052	0,1990	1,1025
0,0767	1,0743	0,0843	1,0619
0,1216	1,0692	0,1268	1,0702
0,1912	1,1086	0,1916	1,0880
0,0696	1,0709	0,0787	1,0458
0,1172	1,0760	0,1271	1,0576
0,1839	1,0880	0,1873	1,0761
0,1635	0,9903	0,1608	0,9750
0,2030	1,0212	0,2016	0,9984
0,2649	1,0452	0,2633	1,0368
0,1381	0,9715	0,1471	0,9607
0,1946	1,0041	0,1949	0,9892
0,2453	1,0469	0,2523	1,0252
0,1306	0,9681	0,1403	0,9493
0,1707	1,0161	0,1881	0,9788
0,2356	1,0606	0,2466	1,0168

Resin Phase			
Mole/ℓ Resin			
Experimental		Fitted	
ΣU	ΣSO_4	ΣU	ΣSO_4
0,2125	1,1805	0,1919	1,1744
0,3035	1,1977	0,2750	1,1939
0,4307	1,2885	-	-
0,2417	1,1189	0,2197	1,1630
0,3311	1,1206	0,3024	1,179
0,4578	1,2465	-	-
0,2568	1,0657	0,2548	1,1097
0,3417	1,0520	0,3288	1,1468
0,4693	1,1634	-	-
0,3119	1,0657	0,2976	1,1056
0,3985	1,0974	0,3705	1,1508
0,5379	1,2268	-	-
0,3046	1,0298	0,3054	1,0614
0,3869	1,1000	0,3681	1,1103
0,5124	1,1874	-	-

Table F.16 Comparison of experimental and fitted concentrations of total sulphate and uranium on resin phase using the Wilson parameters and equilibrium constants quoted in Table 6.5 for system Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 at 298°K. Capacity assumed as 1,4 equiv./l resin. This data is presented graphically in Figure 6.7.

Resin Phase					Experimental				Fitted			
Mole Fraction					HSO_4	$UO_2(SO_4)_3$	$UO_2(SO_4)_2$	NO_3	HSO_4	$UO_2(SO_4)_3$	$UO_2(SO_4)_2$	NO_3
SO_4*	HSO_4*	$UO_2(SO_4)_3$*	$UO_2(SO_4)_2$*	NO_3	λ_{SO_4}	λ_{SO_4}	λ_{SO_4}	λ_{SO_4}	λ_{SO_4}	λ_{SO_4}	λ_{SO_4}	λ_{SO_4}
0,2680	0,2118	0,11601	0,06247	0,3418	5,392	3999,6	49,12	84,51	4,450	4670,9	43.74	82,99
0,2019	0,1601	0,07831	0,04217	0,5176	4,056	4716,7	43,63	40,39	3,843	5535,9	39,19	48,68
0,1482	0,1181	0,04195	0,02259	0,6692	2,971	4626,8	31,42	22,30	3,398	6366,8	34,08	33,54
0,1220	0,5931	0,03228	0,01738	0,2352	1,687	3692,0	20,65	29,40	2,087	2948,4	19,29	42,90
0,0974	0,4704	0,01927	0,01038	0,4026	1,344	3487,5	15,56	17,26	2,000	3439,5	18,17	28,55
0,0684	0,3275	0,01103	0,0059	0,5872	0,943	4085,0	12,81	13,03	1,881	3613,2	15,49	20,78
0,2327	0,1840	0,25004	0,13464	0,1986	4,681	2282,1	24,34	131,05	4,212	2141,0	24,90	179,57
0,1979	0,1567	0,20890	0,11249	0,3240	3,980	2626,9	23,83	101,76	3,624	2464,7	24,90	94,38
0,1517	0,1204	0,17444	0,09393	0,4595	3,048	3710,7	25,81	65,91	3,086	2620,6	22,43	55,44
0,1256	0,0998	0,14858	0,08000	0,5460	2,521	4588,8	26,41	49,36	2,804	2726,7	20,72	41,34
0,1069	0,0852	0,12175	0,06556	0,6205	2,145	5157,6	25,28	41,60	2,611	2894,8	19,51	32,97
0,0970	0,0774	0,10555	0,05683	0,6632	1,943	5409,8	24,05	33,14	2,513	3017,3	18,83	29,28

Table F.17 Comparison of experimental and fitted equilibrium quotients using the Wilson parameters quoted in Table 6.8 for system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$, H_2SO_4 and UO_2SO_4 at 298°K. This data is presented graphically in Figures 6.8, 6.9, 6.10 and 6.11.

Resin phase (Mole/ℓ Resin)					
Experimental			Fitted		
ΣU	ΣSO_4	NO_3	ΣU	ΣSO_4	NO_3
0,1492	0,7835	0,2857	0,1542	0,7923	0,2827
0,1144	0,6181	0,4914	0,1114	0,6252	0,5157
0,0700	0,4416	0,7257	0,0623	0,4295	0,7891
0,0567	0,9497	0,2685	0,0406	0,9481	0,2971
0,0358	0,7706	0,4857	0,0236	0,7577	0,5309
0,0215	0,5800	0,7428	0,0109	0,5649	0,7644
0,2545	0,9355	0,1314	0,2529	0,9372	0,1469
0,2324	0,8696	0,2343	0,2353	0,8751	0,2299
0,2136	0,7659	0,3657	0,2057	0,7780	0,3550
0,1938	0,6802	0,4629	0,1801	0,6965	0,4671
0,1716	0,6057	0,5686	0,1573	0,6240	0,5633
0,1546	0,5680	0,6314	0,1368	0,5583	0,6506

Figure F.18 Comparison of experimental and fitted equilibrium resin composition using the Wilson parameters quoted in Table 6.8 for solution conditions stated in Table 6.6 for system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$, H_2SO_4 and UO_2SO_4 at 298°K. Capacity of 1,4 equiv./l resin is applied. This data is graphically presented in Figure 6.12.

Resin Phase (Mole Fraction)					Experimental				Fitted			
SO_4^*	HSO_4^*	$UO_2(SO_4)_3^*$	$UO_2(SO_4)_2^*$	Cl	λ_{HSO_4} / λ_{SO_4}	$\lambda_{UO_2(SO_4)_3}$ / λ_{SO_4}	$\lambda_{UO_2(SO_4)_2}$ / λ_{SO_4}	λ_{Cl} / λ_{SO_4}	λ_{HSO_4} / λ_{SO_4}	$\lambda_{UO_2SO_4)_3}$ / λ_{SO_4}	$\lambda_{UO_2(SO_4)_2}$ / λ_{SO_4}	λ_{Cl} / λ_{SO_4}
0,3728	0,2942	0,16992	0,09150	0,0716	7,504	3036,4	51,87	9,682	6,539	2808,6	41,54	6,194
0,3498	0,2776	0,15149	0,08157	0,1396	7,026	3060,7	49,07	6,195	6,068	2983,0	41,69	5,726
0,3048	0,2417	0,13591	0,07318	0,2444	6,125	3589,8	50,15	5,348	5,304	3068,1	38,17	5,025
0,2518	0,2007	0,09811	0,05283	0,3965	5,050	3746,3	43,23	4,109	4,386	3609,7	37,42	4,086
0,2070	0,1658	0,07162	0,03856	0,5170	4,144	3995,2	37,91	3,646	3,716	4179,3	35,60	3,400
0,1770	0,1423	0,05173	0,02785	0,6011	3,536	3904,1	31,66	3,137	3,327	4914,8	35,11	2,973
0,2754	0,2178	0,28926	0,15575	0,0617	5,540	1884,2	23,78	9,638	5,985	1769,8	22,96	6,146
0,2608	0,2066	0,26857	0,14461	0,1194	5,243	1942,4	23,22	6,021	5,599	1824,4	22,65	5,743
0,2520	0,2002	0,22390	0,12056	0,2033	5,061	1721,7	19,88	4,430	5,112	2024,2	23,78	5,181
0,2124	0,1696	0,17872	0,09624	0,3431	4,255	1910,7	17,32	3,613	4,240	2212,6	22,56	4,270
0,1706	0,1368	0,14943	0,08046	0,4627	3,412	2445,8	19,12	3,512	3,512	2303,9	19,97	3,527
0,1372	0,1105	0,13089	0,07048	0,5510	2,740	3275,2	20,59	3,369	2,996	2325,9	17,36	3,003

Table F.19 Comparison of experimental and fitted equilibrium quotients using the Wilson parameters quoted in Table 6.11 for system Amberlite 400, mixture of Na_2SO_4, NaCl, H_2SO_4 and UO_2SO_4 at 298°K. This data is presented graphically in Figures 6,13, 6.14, 6.15 and 6.16.

Resin phase				
(Mole/ℓ Resin)				
Experimental		Fitted		
ΣU	Cl	ΣU	ΣSO_4	Cl
0,1854	0,0508	0,1831	0,9634	0,0421
0,1730	0,1036	0,1727	0,9197	0,1018
0,1639	0,1916	0,1571	0,8529	0,1934
0,1322	0,3476	0,1306	0,7381	0,3521
0,1056	0,4956	0,1090	0,6432	0,4850
0,0819	0,6188	0,0912	0,5621	0,5981
0,2710	0,0376	0,2691	1,0238	0,0305
0,2616	0,0756	0,2589	0,9899	0,0746
0,2359	0,1392	0,2428	0,9365	0,1444
0,2087	0,2604	0,2140	0,8398	0,2711
0,1894	0,3812	0,1932	0,7547	0,3833
0,1762	0,4820	0,1667	0,6791	0,4833

Figure F.20 Comparison of experimental and fitted equilibrium resin composition using the Wilson parameters quoted in Table 6.11 for solution conditions stated in Table 6.9 for system Amberlite 400, mixture of Na_2SO_4, NaCl, H_2SO_4 and UO_2SO_4 at 298°K. Capacity of 1,4 equiv./l resin is applied. This data is graphically presented in Figure 6.17.

APPENDIX G

COMPILATION OF LITERATURE DATA FOR SYSTEM, STRONG BASE RESIN, MIXTURES OF SULPHATE SALTS, H_2SO_4 AND UO_2SO_4

The published data is presented for comparison with the experimental work reported in Tables G.1, G.2 and G.3.

Unfortunately the solution phase of the published data is generally not completely defined, for example the acid concentration is rarely specified. Further the resin phase composition is not completely specified. Often the total sulphate on the resin is not reported.

The resin samples used Amberlite 400, Dowex 21K and De-Acidite FF are all polystyrene resins with the same functional group $-N(alkyl)_3^+$. Provided the cross-linking of the different resin samples is similar the results expressed as moles per equivalent of resin should compare with this experimental work.

Solution Phase				Resin Phase		Resin Type	Reference
(Mole/ℓ)			pH	Mole / Equiv. Resin			
ΣU	ΣSO_4	H		ΣU	ΣSO_4		
0,0048	0,780	-	1,8	0,1913	0,7725	Amberlite 400	ARDEN AND WOOD (1956)
0,0048	0,509	-	1,8	0,2026	0,7619		
0,0048	0,270	-	1,8	0,2119	0,7619		
0,0048	0,119	-	1,8	0,2278	0,7725		
0,005	-	-	0,52	0,0762	0,8867	De Acidite FF	ARDEN AND WOOD (1956)
0,005	-	-	1,01	0,1583	0,8564		
0,005	-	-	1,32	0,2039	0,8011		
0,005	-	-	1,61	0,2320	0,7928		
0,005	-	-	1,82	0,2392	0,7735		
0,005	-	-	2,01	0,2494	0,7376		
0,0048	0,771	-	2,5	0,2307	0,8204	De Acidite FF	ARDEN AND WOOD (1956)
0,0048	0,266	-	2,5	0,2428	0,7735		
0,0048	0,117	-	2,5	0,2472	0,7459		
0,0048	0,035	-	2,5	0,2569	0,7735		
0,0048	0,011	-	2,5	0,2633	0,7790		
0,0049	0,105	-	1,8	0,2399	0,7426	Amberlite 400	JOHNSON AND WILWARD (1953)
0,0196	0,412	-	1,8	0,2671	0,8086		

Table G.1 Literature equilibrium data for the system strong base resin, mixtures of sulphate salts H_2SO_4 and $UO_2\ SO_4$

Solution Phase				Resin Phase		Resin Type	Reference
(Mole/ℓ)			pH	(Mole/Equiv. Resin)			
ΣU	ΣSO_4	H		ΣU	ΣSO_4		
0,00713	0,40	-	1,8	0,176	-	Amberlite 400	KUNIN (1969)
0,00356	0,40	-	1,8	0,149	-		
0,00107	0,40	-	1,8	0,087	-		
0,00036	0,40	-	1,8	0,055	-		
0,00368	0,370	0,1016	1,70	0,1799	0,5852	Amberlite 400	O'CONNOR (1954)
0,00374	0,414	0,2032	1,32	0,1451	0,6404		
0,00356	0,20	-	1,34	0,163	-	Amberlite 400	KUNIN (1969)
0,00356	0,10	-	1,01	0,170	-		
0,0005	0,195	-	2,0	0,090	-	Dowex 21K	WATSON (1962)
0,001	0,195	-	2,0	0,127	-		
0,002	0,195	-	2,0	0,163	-		
0,003	0,195	-	2,0	0,175	-		
0,004	0,195	-	2,0	0,187	-		
0,0005	0,50	-	2,0	0,070	-		
0,001	0,50	-	2,0	0,105	-		
0,002	0,50	-	2,0	0,132	-		
0,003	0,50	-	2,0	0,147	-		
0,004	0,50	-	2,0	0,159	-		

Table G.2 Literature equilibrium data for the system strong base resin, mixtures of sulphate salts H_2SO_4 and UO_2SO_4.

Solution Phase (M)				
Σ U	0,0005	0,001	0,002	0,005
	Resin Phase (Mole / Equiv. Resin)			
ΣSO_4	ΣU	ΣU	ΣU	ΣU
0,10	0,112	0,145	0,182	0,193
0,15	0,103	0,136	0,171	0,184
0,20	0,097	0,127	0,162	0,180
0,25	0,090	0,118	0,156	0,175
0,30	0,086	0,112	0,151	0,175
0,35	0,081	0,105	0,147	0,175
0,40	0,079	0,101	0,143	0,175
0,45	0,077	0,097	0,140	0,178
0,50	0,079	0,097	0,138	0,180
0,55	0,079	0,097	0,136	0,182
0,60	0,081	0,099	0,132	0,184

Table G.3 Smoothed resin loading data of Stein (1962) for system Dowex 21K, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4 at pH 2.0.

APPENDIX H

IDENTIFICATION OF SPECIES IN RESIN PHASE

An assumption made in this treatment is that the stoichiometry of the complexes in the resin phase is known. This is not easily determined experimentally particularly when more than one complex may coexist in the resin for a particular solution condition.

MARCUS and KERTES (1969) discuss in depth the equivalent accounting method as applied to anionic complexes. Information on species formed in the resin may also be obtained from resin loading. This is important in studies by distribution methods. The authors discuss the application of these methods.

HEITNER-WIRGUIM and BEN-ZWI (1970, 1970) assign the visible and near infrared absorption of cobalt (II) chloride species sorbed on cation and anion ion exchangers by comparing these spectra with those of known species in other media and by taking into account the properties of various ion exchangers used.

POPE and BOEYENS (1975) have determined the crystal structure of S-benzylisothiouronium hexachloroplatinate (IV) and tetrachloroaurate (III) from three dimensional X-ray data obtained from integrated Weissenberg photographs. The S-benzylisothiouronium cation occurs as the functional group in polystyrene resins which are selective for platinum group metals and gold.

HEITNER-WIRGUIM and GANTZ (1973) have identified the uranyl sulphate species sorbed on anion and cation ion exchangers from sulphate solutions by comparing the visible and infrared spectra of the species sorbed with

those of species present in aqueous and non-aqueous phases. The species identified were $UO_2HSO_4^+$, $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$.

MAJCHRZAK (1971) has identified the uranium (VI) complexes sorbed on anion exchange resins from sulphate solutions from their absorption spectra (400-500 nm) and by calculating their composition from the amount of sulphate and uranium absorbed. At low uranium, less than 10 mmol/litre the two complexes $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$ are sorbed. At high uranium with an excess of sulphate both complexes are absorbed, however at low sulphate $UO_2(SO_4)_2^{2-}$ prevails.

Similarly MAJCHRZAK (1969) has identified the uranium (VI) complexes sorbed on ion exchange resins from carbonate solutions. The complex $UO_2(CO_3)_3^{4-}$ is the only complex formed when the carbonate concentration is high.

YOSHIMURA *et al* employ the 'indifferent electrolyte adding' method to determine the predominant species absorbed from uranyl nitrate, sodium nitrate solutions. At solution nitrate concentrations of 2M $UO_2(NO_3)_3^-$ predominates and at 4-6M $UO_2)NO_3)_4^{2-}$ predominates. The coexistence of the two species is presumed at 2-4 M nitrate.

APPENDIX I

NUMERICAL METHODS

One of two unconstrained minimisation routines is used depending on the number of functions, that is the number of independent reactions or parameters considered.

I.1 SUBROUTINE NELM

This subroutine finds the unconstrained minimum of a single function of several variables F(X) where X is the vector X(1) -- X(N). This method described by NELDER and MEAD (1965) makes use of the geometrical simplex which is defined by n + 1 noncoplanar points in n dimensional space.

I.2 SUBROUTINE VA02A

For two or more functions this subroutine minimises the sum of squares F of M given functions of N variables.

$$F(X_1, X_2, \ldots\ldots, X_N) = \sum_{j=1}^{M} f_i(X_1, X_2, \ldots\ldots, X_N)^2 \qquad M \geq N$$

This method described by POWELL (1965) unlike the classical procedure does not require any derivatives.

Both routines NELM and VA02A require a subroutine CALFUN which is user written to calculate the functions to be minimised.

APPENDIX J

COMPUTER PROGRAMS AND SPECIMEN CALCULATIONS

J.1 PARAMETER ESTIMATION

The program WILMOLF is used to estimate the Wilson interaction coefficients Λ_{ij} and the equilibrium constants K_i as outlined in Section 3.7.

The minimisation routine VA02A is used in this program.

J.1.1 Specimen calculations

The results for the ternary system Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and $NaNO_3$ are presented in Table J.1. In this case both equilibrium constants are specified from the characterisation of previous subsystems. Two interaction parameters are estimated.

J.2 SOLUTION OF SIMULTANEOUS NON-LINEAR EQUATIONS

The general program DISTRIB is used to solve the simultaneous equations for the equilibrium extents. The minimisation routine NELM is used for one equation while VA02A is used for more than one equation.

J.2.1 Specimen calculations

A. Solution phase activities

The activities of the solution phase species for at least one experimental condition of the following systems have been determined

(a)	mixture of Na_2SO_4 and $NaNO_3$	Table J.2
(b)	mixture of Na_2SO_4, $NaNO_3$ and NaCl	Table J.3
(c)	mixture of Na_2SO_4, $NaNO_3$, NaCl and H_2SO_4	Table J.4
(d)	mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4	Table J.5
(e)	mixture of Na_2SO_4, $NaNO_3$, NaCl, H_2SO_4 and UO_2SO_4.	Table J.6

Program DISTRIB with NOPTION = 1 is used.

B. Fitted resin phase composition

The fitted resin phase compositions for the following systems have been determined

(a)	binary system SO_4^{2-} - NO_3^-	Table J.7
(b)	binary system SO_4^{2-} - HSO_4^-	Table J.8
(c)	quaternary system SO_4^{2-} - HSO_4^- - $UO_2(SO_4)_3^{4-}$ - $UO_2(SO_4)_2^{2-}$	Table J.9

for one experimental condition. Program DISTRIB with NOPTION = 2 is used.

C. Predicted resin phase composition

For the activities determined in Section A the predictions of the resin phase composition for the following systems are presented

(a)	SO_4^{2-} - NO_3^- - Cl^-	Table J.10
(b)	SO_4^{2-} - HSO_4^- - NO_3^- - Cl^-	Table J.11
(c)	SO_4^{2-} - HSO_4^- - $UO_2(SO_4)_3^{4-}$ - $UO_2(SO_4)_2^{2-}$ - NO_3^- - Cl^-	Table J.12

Program DISTRIB with NOPTION = 2 is used.

J.3 ACTIVITIES OF SPECIES IN NON-COMPLEX SYSTEMS

The program NOCOMP is used to calculate the activities of solution species in non-complex systems from the extended Debye-Huckel equation. A few results for the system NaCl and $NaNO_3$ have been presented as specimen calculations in Table J.13.

J.4 SPECIMEN CALCULATION OF THE EQUILIBRIUM QUOTIENT

A. Equilibrium quotient for the system SO_4^{2-} - NO_3^-

Taking the first experiment as an example from Table F.3 the mole fractions of the species are

$$x_{NO_3} = 0,599$$

$$x_{SO_4} = 0,401$$

From the printout Table J.2 the activities of the solution species for the corresponding experiment are

$$a'_{SO_4} = 0,01926$$

$$a'_{NO_3} = 0,01349$$

From Equation (4.3) the equilibrium quotient is given by

$$\lambda_{SO_4}^{NO_3} = \frac{(0,599)^2 (0,01926)}{(0,401)\ (0,01349)^2}$$

$$\lambda_{SO_4}^{NO_3} = 94,68$$

B. Equilibrium quotients for the quaternary system
SO_4^{2-} - HSO_4^- - $UO_2(SO_4)_3^{4-}$ - $UO_2(SO_4)_2^{2-}$

Using the first experiment of this series as an example the mole fractions of the resin species are given from Table F.13

$x_{SO_4} = 0,4978$

$x_{HSO_4} = 0,3613$

$x_{UO_2(SO_4)_3} = 0,09158$

$x_{UO_2(SO_4)_2} = 0,04931$

From the printout Table J.5 the activities of the solution species for the corresponding experiment are

$a'_H = 0,009259$ and pH = 2,03

$a'_{SO_4} = 0,035523$

$a'_{HSO_4} = 0,029996$

$a'_{UO_2SO_4} = 0,79857 \times 10^{-4}$

$a'_{UO_2(SO_4)_2} = 0,333296 \times 10^{-4}$

From Equation (6.8) the equilibrium quotients are

$$\lambda_{SO_4}^{HSO_4} = \frac{(0,3613)^2\ (0,035523)}{(0,4978)\quad (0,029996)^2} = 10,35$$

$$\lambda_{SO_4}^{UO_2(SO_4)_3} = \frac{(0,09158)}{(0,4978)^2\ (0,79858 \times 10^{-4})} = 4627,7$$

$$\lambda_{SO_4}^{UO_2(SO_4)_2} = \frac{(0,04931)\ (0,035523)}{(0,4978)(0,333296 \times 10^{-4})} = 105,57$$

```
FILE  2 =  INPUT              ,UNIT = READER                                    R  0000
FILE  3 =  OUTPUT             ,UNIT = PRINTER                                   R  0000
                                                        START OF SEGMENT **********    1
      COMMON Y(200,4),CKS(200),BETA(3,4),XLAMDA(4,4),GAMMA(4),CKSTAR(200        R  0000
     1),NCOMP,CKT(3),NREA,DEL(4,4)                                              R  0000
      DIMENSION F(200),X(15),W(10000),E(15)                                     R  0000
      DIMENSION NEX(200)                                                        R  0000
      READ(2,2001) NFLAG                                                        R  0000
 2001 FORMAT(I5)                                                                R  0010
      READ(2,100) NCOMP,NREA                                                    R  0010
  100 FORMAT(2I5)                                                               R  0024
      WRITE(3,200) NCOMP,NREA                                                   R  0024
  200 FORMAT(5X,18HNO OF COMPONENTS =,I5,5X,17HNO OF REACTIONS =,I5)            R  0038
      READ(2,100)M,N                                                            R  0038
      WRITE(3,201)M,N                                                           R  0049
  201 FORMAT(//5X,17HNO OF DATA SETS =,I5,5X,18HNO OF PARAMETERS =,I5)          R  0062
      READ(2,100) IPRINT,MAXFUN                                                 R  0062
      READ(2,102) ESCALE                                                        R  0073
      WRITE(3,202) IPRINT,MAXFUN,ESCALE                                         R  0083
  202 FORMAT(5X,2I5,E10.3)                                                      R  0095
  102 FORMAT(E10.3)                                                             R  0098
      READ(2,103)(E(I),I=1,N)                                                   R  0098
      READ(2,103)(X(I),I=1,N)                                                   R  0115
  103 FORMAT(6E12.5)                                                            R  0132
      WRITE(3,203)                                                              R  0132
  203 FORMAT(//5X,23HTOLERANCE ON PARAMETERS)                                   R  0136
      WRITE(3,103)(E(I),I=1,N)                                                  R  0136
      WRITE(3,204)                                                              R  0153
  204 FORMAT(//5X,15HINITIAL GUESSES)                                           R  0157
      WRITE(3,103)(X(I),I=1,N)                                                  R  0157
```

```
      DO 2 I=1,NREA                                                    R  0174
      READ(2,104)(BETA(I,J),J=1,NCOMP)                                 R  0180
2     CONTINUE                                                         R  0203
104   FORMAT(4F5.3)                                                    R  0204
      WRITE(3,1005)                                                    R  0204
1005  FORMAT(//50X,9HCOMPONENT)                                        R  0208
      WRITE(3,1006)                                                    R  0208
1006  FORMAT(2X,11HREACTION(I))                                        R  0212
      WRITE(3,1007)(J,J=1,NCOMP)                                       R  0212
1007  FORMAT(13X,20I5)                                                 R  0229
      DO 7 I=1,NREA                                                    R  0229
      WRITE(3,1008)I,(BETA(I,J),J=1,NCOMP)                             R  0235
1008  FORMAT(5X,I5,5X,20F5.2)                                          R  0260
7     CONTINUE                                                         R  0260
      DO 10 K=1,M                                                      R  0260
      READ(2,2000) NEX(K),CKS(K),(Y(K,I),I=1,NCOMP)                    R  0265
2000  FORMAT(1X,I6,5X,5E12.5)                                          R  0297
10    CONTINUE                                                         R  0297
      IF(NFLAG.EQ.0)GO TO 20                                           R  0297
      WRITE(3,3000)                                                    R  0299
3000  FORMAT(//1X,10HEXP NUMBER,2X,9HEQU RATIO,2X,29HEQUIVALENT FRACTION  R  0304
     1S ON RESIN,//40X,9HCOMPONENT)                                    R  0304
      GO TO 21                                                         R  0304
20    WRITE(3,3005)                                                    R  0305
3005  FORMAT(//1X,10HEXP NUMBER,2X,9HEQU RATIO,8X,23HMOLE FRACTION ON RE  R  0309
     1SIN,//40X,9HCOMPONENT)                                           R  0309
21    WRITE(3,3001)(J,J=1,NCOMP)                                       R  0309
3001  FORMAT(/19X,4(10X,I2))                                           R  0326
      DO 11 K=1,M                                                      R  0326
      WRITE(3,2000) NEX(K),CKS(K),(Y(K,I),I=1,NCOMP)                   R  0331
11    CONTINUE                                                         R  0363
      CALL VA02A(M,N,F,X,L,ESCALE,IPRINT,MAXFUN)                       R  0363
      WRITE(3,3003)                                                    R  0363
3003  FORMAT(//1X,7HEXP NUM,2X,12HEQ RATIO EXP,2X,13HEQ RATIO CALC,7X,14  R  0372
     1HFRACTION RESIN,36X,14HACT COEFF CALC,//48X,9HCOMPONENT,36X,9HCOMP  R  0372
     1ONENT)                                                           R  0372
                                                        SEGMENT    2 IS  120 LONG
      WRITE(3,3006)(J,J=1,NCOMP),(I,I=1,NCOMP)                         R  0372
3006  FORMAT(/26X,4(10X,I2),4(10X,I2))                                 R  0399
      DO 4 K=1,M                                                       R  0399
      CALL RGAMMA(K)                                                   R  0404
```

```
      WRITE(3,3007)NEX(K),CKS(K),CKSTAR(K),(Y(K,I),I=1,NCOMP),(GAMMA(I),     R  0405
     1I=1,NCOMP)                                                             R  0449
 3007 FORMAT(1X,I6,10E12.5)                                                  R  0459
 4    CONTINUE                                                               R  0459
      WRITE(3,3008)                                                          R  0459
 3008 FORMAT(//1X,11HREACTION NO,4X,22HTHERMODYNAMIC CONSTANT)               R  0463
      DO 5 I=1,NREA                                                          R  0463
      WRITE(3,3009)I,CKT(I)                                                  R  0469
 5    CONTINUE                                                               R  0487
 3009 FORMAT(5X,I5,12X,E12.5)                                                R  0488
      WRITE(3,3010)                                                          R  0488
 3010 FORMAT(//1X,23HPARAMETERS " LAMDA(I,J))                                R  0492
      WRITE(3,3011)(J,J=1,NCOMP)                                             R  0492
 3011 FORMAT(/1X,9HCOMPONENT,4(10X,I2))                                      R  0509
      DO 6 I=1,NCOMP                                                         R  0509
      WRITE(3,3012)I,(XLAMDA(I,J),J=1,NCOMP)                                 R  0515
 3012 FORMAT(/5X,I2,9X,4E12.5)                                               R  0540
 6    CONTINUE                                                               R  0540
      STOP                                                                   R  0540
      END                                                                    R  0542
```

SEGMENT 1 IS 557 LONG

START OF SEGMENT ********** 3

```
      SUBROUTINE CALFUN(M,N,F,X)                                             R  0000
      COMMON Y(200,4),CKS(200),BETA(3,4),XLAMDA(4,4),GAMMA(4),CKSTAR(200     R  0000
     1),NCOMP,CKT(3),NREA,DEL(4,4)                                           R  0000
      DIMENSION F(200),X(15),W(10000),E(15)                                  R  0000
      DO 120 I=1,NCOMP                                                       R  0000
      XLAMDA(I,I) = 1.0                                                      R  0006
 120  CONTINUE                                                               R  0014
      CKT(1) = 5.098                                                         R  0014
      CKT(2) = 72.939                                                        R  0018
      XLAMDA(1,2) = 0.9846                                                   R  0022
      XLAMDA(1,3) = 0.65419                                                  R  0026
      XLAMDA(2,1) = 2.8124                                                   R  0030
      XLAMDA(2,3) = EXP(X(1))                                                R  0034
      XLAMDA(3,1) = 3.1159                                                   R  0037
      XLAMDA(3,2) = EXP(X(2))                                                R  0041
      NPER=M/NREA                                                            R  0044
      DO 100 K=1,M                                                           R  0047
      CALL RGAMMA(K)                                                         R  0052
```

```
      IF(K.GE.NPER+1) NNR=2                                          R  0055
      IF(K.GE.2*NPER+1) NNR=3                                        R  0053
      CKSTAR(K) = CKT(NNR)                                           R  0061
      DO 110 J=1,NCOMP                                               R  0072
      CKSTAR(K) = CKSTAR(K)/GAMMA(J)**BETA(NNR,J)                    R  0078
  110 CONTINUE                                                       R  0101
      F(K) = (CKS(K)-CKSTAR(K))/CKS(K)                               R  0101
  100 CONTINUE                                                       R  0117
      RETURN                                                         R  0117
      END                                                            R  0120
                                                    SEGMENT     3 IS   131 LONG
```

```
                                                    START OF SEGMENT **********    4
      SUBROUTINE RGAMMA(K)                                           R  0000
      COMMON Y(200,4),CKS(200),BETA(3,4),XLAMDA(4,4),GAMMA(4),CKSTAR(200  R  0000
     1),NCOMP,CKT(3),NREA,DEL(4,4)                                   R  0000
      DIMENSION F(200),X(15),M(10000),E(15)                          R  0000
      DO 100 I=1,NCOMP                                               R  0000
      XLSUM=0.0                                                      R  0006
      XSUM1=0.0                                                      R  0007
      DO 70 J=1,NCOMP                                                R  0008
      XLSUM=XLSUM+Y(K,J)*XLAMDA(I,J)                                 R  0014
      XSUM2=0.0                                                      R  0025
      DO 60 M=1,NCOMP                                                R  0025
      XSUM2=XSUM2+Y(K,M)*XLAMDA(J,M)                                 R  0032
   60 CONTINUE                                                       R  0043
      XSUM1=XSUM1+Y(K,J)*XLAMDA(J,I)/XSUM2                           R  0043
   70 CONTINUE                                                       R  0055
      GAMMA(I) = EXP(1.0-XSUM1)/XLSUM                                R  0055
  100 CONTINUE                                                       R  0065
      RETURN                                                         R  0065
      END                                                            R  0068
```

```
                                                                  START OF SEGMENT **********    5
      SUBROUTINE VA02A(M,N,F,X,E,ESCALE,IPRINT,MAXFUN)                                    P  0000
      COMMON/VDD/XINC,IINC,FA,FB,D,DA,DB,DC,IZ,FZ                                         R  0000
      DIMENSION F(200),X(15),W(10000),E(15)                                               R  0000
      MPLUSN=M+N                                                                          R  0000
      KST=N+MPLUSN                                                                        R  0001
      NPLUS=N+1                                                                           R  0002
      KINV=NPLUS*(NPLUSN+1)                                                               R  0003
      KSTORE=KINV-MPLUSN-1                                                                P  0005
      CALL CALFUN(M,N,F,X)                                                                R  0007
      NN=N+N                                                                              P  0010
      K=NN                                                                                R  0011
      DO1 I=1,M                                                                           R  0012
      K=K+1                                                                               R  0017
      W(K)=F(I)                                                                           R  0019
    1 CONTINUE                                                                            R  0025
      IINV=2                                                                              R  0025
      K=KST                                                                               R  0026
      I=1                                                                                 R  0027
    2 X(I)=X(I)+E(I)                                                                      R  0028
      CALL CALFUN(M,N,F,X)                                                                R  0033
      X(I)=X(I)-E(I)                                                                      R  0036
      DO 3 J=1,N                                                                          R  0041
      K=K+1                                                                               R  0046
      W(K)=0.                                                                             R  0048
      W(J)=0.                                                                             R  0052
    3 CONTINUE                                                                            R  0057
      SUM=0.                                                                              R  0057
      KK=NN                                                                               R  0058
      DO 4 J=1,M                                                                          R  0059
      KK=KK+1                                                                             R  0064
      F(J)=F(J)-W(KK)                                                                     R  0066
      SUM=SUM+F(J)*F(J)                                                                   R  0073
    4 CONTINUE                                                                            R  0078
      IF (SUM) 5,5,6                                                                      R  0078
    5 WRITE(3,7)I                                                                         R  0081
    7 FORMAT(5X,9HVA02A  E(,I3,20H) UNREASONABLY SMALL.  )                                R  0091
      DO 8 J=1,M                                                                          R  0091
      NN=NN+1                                                                             R  0096
      F(J)=W(NN)                                                                          R  0098
```

```
  8 CONTINUE                                                        R  0104
    GO TO 10                                                        R  0104
  6 SUM=1./SQRT(SUM)                                                R  0106
    J=K-N+I                                                         R  0107
    W(J)=E(I)*SUM                                                   R  0109
    DO 9 J=1,M                                                      R  0115
    K=K+1                                                           R  0120
    W(K)=F(J)*SUM                                                   R  0122
    KK=NN+J                                                         R  0128
    DO 11 II=1,I                                                    R  0129
    KK=KK+MPLUSN                                                    R  0134
    W(II)=W(II)+W(KK)*W(K)                                          R  0136
 11 CONTINUE                                                        R  0151
  9 CONTINUE                                                        R  0152
    ILESS=I-1                                                       R  0152
    IGAMAX=N+I-1                                                    R  0153
    INCINV=N-ILESS                                                  R  0155
    INCINP=INCINV+1                                                 R  0156
    IF (ILESS) 13,13,14                                             R  0158
 13 W(KINV)=1.                                                      R  0161
    GO TO 15                                                        R  0165
 14 B=1.                                                            R  0166
    DO 16 J=NPLUS,IGAMAX                                            R  0166
    W(J)=0.                                                         R  0172
 16 CONTINUE                                                        R  0177
    KK=KINV                                                         R  0177
    DO 17 II=1,ILESS                                                R  0178
    IIP=II+N                                                        R  0183
    W(IIP)=W(IIP)+W(KK)*W(II)                                       R  0185
    JL=II+1                                                         R  0200
    IF (JL-ILESS) 18,18,19                                          R  0201
 18 DO 20 JJ=JL,ILESS                                               R  0204
    KK=KK+1                                                         R  0209
    JJP=JJ+N                                                        R  0211
    W(IIP)=W(IIP)+W(KK)*W(JJ)                                       R  0212
    W(JJP)=W(JJP)+W(KK)*W(II)                                       R  0227
 20 CONTINUE                                                        R  0243
 19 B=B-W(II)*W(IIP)                                                R  0244
```

```
      KK=KK+INCINP                                                      R  0252
   17 CONTINUE                                                          R  0254
      B=1./B                                                            R  0254
      KK=KINV                                                           R  0255
      DO 21 II=NPLUS,IGAMAX                                             R  0256
      BB=-B*W(II)                                                       R  0261
      DO 22 JJ=II,IGAMAX                                                R  0266
      W(KK)=W(KK)-BB*W(JJ)                                              R  0271
      KK=KK+1                                                           R  0283
   22 CONTINUE                                                          R  0285
      W(KK)=BB                                                          R  0285
      KK=KK+INCINV                                                      R  0289
   21 CONTINUE                                                          R  0291
      W(KK)=B                                                           R  0291
   15 GO TO (27,24),IINV                                                R  0296
   24 I=I+1                                                             R  0302
      IF (I-N) 2,2,25                                                   R  0303
   25 IINV=1                                                            R  0306
      FF=0.                                                             R  0306
      KL=NN                                                             R  0307
      DO 26 I=1,M                                                       R  0308
      KL=KL+1                                                           R  0313
      F(I)=W(KL)                                                        R  0315
      FF=FF+F(I)*F(I)                                                   R  0320
   26 CONTINUE                                                          R  0325
      ICONT=1                                                           R  0325
      ISS=1                                                             R  0326
      MC=N+1                                                            R  0327
      IPP=IABS(IPRINT)*(IABS(IPRINT)-1)                                 R  0328
      ITC=0                                                             R  0330
      IPS=1                                                             R  0331
      IPC=0                                                             R  0332
   27 IPC=IPC-IABS(IPRINT)                                              R  0333
      IF (IPC) 28,29,29                                                 R  0334
   28 WRITE(3,30) ITC,MC,FF                                             R  0337
   30 FORMAT (//5X,9HITERATION,I4,I9,16H CALLS OF CALFUN,5X,2HF=,E24.14) R  0351
      WRITE(3,31)(X(I),I=1,N)                                           R  0351
   31 FORMAT (5X,9HVARIABLES,/(5E24.14))                                R  0369
      IF(IPRINT)1000,1001,1001                                          R  0369
 1001 WRITE(3,32)(F(I),I=1,M)                                           R  0372
   32 FORMAT (5X,9HFUNCTIONS,/(5E24.14))                                R  0390
 1000 IPC=IPP                                                           R  0390
```

```
      GO TO (29,33),IPS                                                  R  0390
   29 GO TO (34,35),ICONT                                                R  0397
   35 IF (CHANGE-1.) 10,10,36                                            R  0403
   10 IF(IPRINT)1003,33,37                                               R  0406
 1003 WRITE(3,1002)                                                      R  0411
 1002 FORMAT(//5X,31HVA02A FINAL VALUES OF VARIABLES)                    R  0415
      GO TO 1004                                                         R  0415
   37 WRITE(3,38)                                                        R  0416
   38 FORMAT (//5X,45HVA02A FINAL VALUES OF FUNCTIONS AND VARIABLES)     R  0420
                                                          SEGMENT    *6 IS   121 LONG
 1004 IPS=2                                                              R  0420
      GO TO 28                                                           R  0420
   33 RETURN                                                             R  0422
   36 ICONT=1                                                            R  0425
   34 ITC=ITC+1                                                          R  0426
      K=N                                                                R  0427
      KK=KST                                                             R  0428
      DO 39 I=1,N                                                        R  0429
      K=K+1                                                              R  0434
      W(K)=0.                                                            R  0435
      KK=KK+N                                                            R  0440
      W(I)=0.                                                            R  0441
      DO 40 J=1,M                                                        R  0445
      KK=KK+1                                                            R  0451
      W(I)=W(I)+W(KK)*F(J)                                               R  0453
   40 CONTINUE                                                           R  0466
   39 CONTINUE                                                           R  0467
      DM=0.                                                              R  0467
      K=KINV                                                             R  0468
      DO 41 II=1,N                                                       R  0469
      IIP=II+N                                                           R  0474
      W(IIP)=W(IIP)+W(K)*W(II)                                           R  0476
      JL=II+1                                                            R  0491
      IF (JL-N) 42,42,43                                                 R  0492
   42 DO 44 JJ=JL,N                                                      R  0495
      JJP=JJ+N                                                           R  0500
      K=K+1                                                              R  0502
      W(IIP)=W(IIP)+W(K)*W(JJ)                                           R  0503
      W(JJP)=W(JJP)+W(K)*W(II)                                           R  0514
   44 CONTINUE                                                           R  0534
      K=K+1                                                              R  0534
   43 IF (DM-ABS(W(II)*W(IIP))) 45,41,41                                 R  0536
```

```
 45 DM=ABS(W(II)*W(IIP))                                                R  0546
    KL=II                                                               R  0554
 41 CONTINUE                                                            R  0555
    II=N+MPLUSN*KL                                                      R  0555
    CHANGE=0.                                                           R  0557
    DO 46 I=1,N                                                         R  0558
    JL=N+I                                                              R  0563
    W(I)=0.                                                             R  0565
    DO 47 J=NPLUS,NN                                                    R  0569
    JL=JL+MPLUSN                                                        R  0574
    W(I)=W(I)+W(J)*W(JL)                                                R  0575
 47 CONTINUE                                                            R  0591
    II=II+1                                                             R  0591
    W(II)=W(JL)                                                         R  0592
    W(JL)=X(I)                                                          R  0600
    IF (ABS(E(I)*CHANGE)-ABS(W(I))) 48,48,46                            R  0605
 48 CHANGE=ABS(W(I)/E(I))                                               R  0614
 46 CONTINUE                                                            R  0620
    DO 49 I=1,M                                                         R  0620
    II=II+1                                                             R  0625
    JL=JL+1                                                             R  0627
    W(II)=W(JL)                                                         R  0628
    W(JL)=F(I)                                                          R  0635
 49 CONTINUE                                                            R  0642
    FC=FF                                                               R  0642
    ACC=0.1/CHANGE                                                      R  0643
    IT=3                                                                R  0646
    XC=0.                                                               R  0646
    XL=0.                                                               R  0647
    IS=3                                                                R  0648
    XSTEP=-AMIN1(0.5,ESCALE/CHANGE)                                     R  0649
    IF (CHANGE-1.) 50,50,51                                             R  0656
 50 ICONT=2                                                             R  0659
 51 CALL VD01A (IT,XC,FC,6,ACC,0.1,XSTEP)                               R  0660
    GO TO (52,53,53,53),IT                                              R  0664
 52 MC=MC+1                                                             R  0672
    IF (MC-MAXFUN) 54,54,55                                             R  0673
 55 WRITE(3,56)MAXFUN                                                   R  0676
 56 FORMAT(5X,5HVA02A,I6,17H  CALLS OF CALFUN)                          R  0686
    ISS=2                                                               R  0686
    GO TO 53                                                            R  0686
 54 XL=XC-XL                                                            R  0688
```

```
      DO 57 J=1,N                                                       R  0689
      X(J)=X(J)+XL*W(J)                                                 R  0694
   57 CONTINUE                                                          R  0703
      XL=XC                                                             R  0703
      CALL CALFUN(M,N,F,X)                                              R  0704
      FC=0.                                                             R  0707
      DO 58 J=1,M                                                       R  0708
      FC=FC+F(J)*F(J)                                                   R  0713
   58 CONTINUE                                                          R  0718
      GO TO (59,59,60),IS                                               R  0718
   60 K=N                                                               R  0725
      IF (FC-FF) 61,51,62                                               R  0725
   61 IS=2                                                              R  0731
      FMIN=FC                                                           R  0731
      FSEC=FF                                                           R  0732
      GO TO 63                                                          R  0733
   62 IS=1                                                              R  0734
      FMIN=FF                                                           R  0734
      FSEC=FC                                                           R  0735
      GO TO 63                                                          R  0736
   59 IF (FC-FSEC) 64,51,51                                             R  0737
   64 K=KSTORE                                                          R  0740
      GO TO (75,74),IS                                                  R  0740
   75 K=N                                                               R  0747
   74 IF (FC-FMIN) 65,51,66                                             R  0748
   66 FSEC=FC                                                           R  0753
      GO TO 63                                                          R  0753
   65 IS=3-IS                                                           R  0755
      FSEC=FMIN                                                         R  0756
      FMIN=FC                                                           R  0757
   63 DO 67 J=1,N                                                       R  0758
      K=K+1                                                             R  0763
      W(K)=X(J)                                                         R  0765
   67 CONTINUE                                                          R  0771
      DO 68 J=1,M                                                       R  0771
      K=K+1                                                             R  0776
      W(K)=F(J)                                                         R  0778
68    CONTINUE                                                          R  0784
      GO TO 51                                                          R  0784
   53 K=KSTORE                                                          R  0785
      KK=N                                                              R  0785
```

```
      GO TO (69,70,69),IS                                          R  0786
   70 K=N                                                          R  0793
      KK=KSTORE                                                    R  0793
   69 SUM=0.                                                       R  0795
      DM=0.                                                        R  0795
      JJ=KSTORE                                                    R  0796
      DO 71 J=1,N                                                  R  0797
      K=K+1                                                        R  0802
      KK=KK+1                                                      R  0804
      JJ=JJ+1                                                      R  0805
      X(J)=W(K)                                                    R  0806
      W(JJ)=W(K)*W(KK)                                             R  0812
   71 CONTINUE                                                     R  0824
      DO 72 J=1,M                                                  R  0824
      K=K+1                                                        R  0829
      KK=KK+1                                                      R  0831
      JJ=JJ+1                                                      R  0832
      F(J)=W(K)                                                    R  0833
      W(JJ)=W(K)*W(KK)                                             R  0839
      SUM=SUM+W(JJ)*W(JJ)                                          R  0850
      DM=DM+F(J)*W(JJ)                                             R  0858
   72 CONTINUE                                                     R  0865
      GO TO (73,10),ISS                                            R  0865
   73 J=KINV                                                       R  0871
      KK=NPLUS-KL                                                  R  0871
      DO 76 I=1,KL                                                 R  0873
      K=J+KL-I                                                     R  0878
      J=K+KK                                                       R  0880
      W(I)=W(K)                                                    R  0881
      W(K)=W(J-1)                                                  R  0889
   76 CONTINUE                                                     R  0899
      IF (KL-N) 77,78,78                                           R  0898
   77 KL=KL+1                                                      R  0902
      JJ=K                                                         R  0903
      DO 79 I=KL,N                                                 R  0904
      K=K+1                                                        R  0909
      J=J+NPLUS-I                                                  R  0911
      W(I)=W(K)                                                    R  0912
      W(K)=W(J-1)                                                  R  0920
   79 CONTINUE                                                     R  0929
      W(JJ)=W(K)                                                   R  0929
      S=1./W(KL-1)                                                 R  0937
```

```
      W(KL-1)=W(N)
   78 B=1./W(N)
      GO TO 88
   88 K=KINV
      DO 80 I=1,ILESS
      BB=B*W(I)
      DO 81 J=I,ILESS
      W(K)=W(K)-BB*W(J)
      K=K+1
   81 CONTINUE
      K=K+1
   80 CONTINUE
      IF (FMIN-FF) 82,83,83
   83 CHANGE=0.
      GO TO 84
   82 FF=FMIN
      CHANGE=ABS(XC)*CHANGE
   84 XL=.0M/FMIN
      SUM=1./SQRT(SUM+DM*XL)
      K=KSTORE
      DO 85 I=1,N
      K=K+1
      W(K)=SUM*W(K)
      W(I)=0.
   85 CONTINUE


      DO 86 I=1,M
      K=K+1
      W(K)=SUM*(W(K)+XL*F(I))
      KK=IN+I
      DO 87 J=1,N
      KK=KK+MPLUSN
      W(J)=W(J)+W(KK)*W(K)
   87 CONTINUE
   86 CONTINUE
      GO TO 14
      END
```

```
                                R  0942
                                R  0950
                                R  0954
                                R  0956
                                R  0956
                                R  0962
                                R  0967
                                R  0972
                                R  0984
                                R  0986
                                R  0986
                                R  0988
                                R  0988
                                R  0992
                                R  0992
                                R  0994
                                R  0994
                                R  0997
                                R  0998
                                R  1001
                                R  1002
                                R  1007
                                R  1009
                                R  1017
                                R  1022
        SEGMENT     5 IS 1023 LONG
START OF SEGMENT ********** 7
                                R  0001
                                R  0006
                                R  0008
                                R  0018
                                R  0019
                                R  0024
                                R  0026
                                R  0041
                                R  0042
                                R  0042
                                R  0043
        SEGMENT     7 IS   74 LONG
```

```
                                                                START OF SEGMENT **********    8
      SUBROUTINE VD01A(ITEST,X,F,MAXFUN,ABSACC,RELACC,XSTEP)                    R  0000
      COMMON/VD0/XINC,IINC,FA,FB,D,DA,DB,DC,IS,FC                               R  0000
      GO TO (1,2,2),ITEST                                                       R  0000
    2 IS=6-ITEST                                                                R  0007
      ITEST=1                                                                   R  0008
      IINC=1                                                                    R  0009
      XINC=XSTEP+XSTEP                                                          R  0010
      MC=IS-3                                                                   R  0011
      IF(MC)4,4,15                                                              R  0013
    3 MC=MC+1                                                                   R  0016
      IF(MAXFUN-MC)12,15,15                                                     R  0017
   12 ITEST=4                                                                   R  0020
   43 X=DB                                                                      R  0021
      F=FB                                                                      R  0022
      IF(FB-FC)15,15,44                                                         R  0023
   44 X=DC                                                                      R  0027
      F=FC                                                                      R  0028
   15 RETURN                                                                    R  0029
    1 GO TO (5,6,7,8),IS                                                        R  0032
    8 IS=3                                                                      R  0040
    4 DC=X                                                                      R  0041
      FC=F                                                                      R  0042
      X=X+XSTEP                                                                 R  0043
      GO TO 3                                                                   R  0044
    7 IF(FC-F)9,10,11                                                           R  0045
   10 X=X+XINC                                                                  R  0051
      XINC=XINC+XINC                                                            R  0052
      GO TO 3                                                                   R  0054
    9 DB=X                                                                      R  0055
      FB=F                                                                      R  0056
      XINC=-XINC                                                                R  0057
      GO TO 13                                                                  R  0058
   11 DB=DC                                                                     R  0060
      FB=FC                                                                     R  0061
      DC=X                                                                      R  0062
      FC=F                                                                      R  0063
   13 X=DC+DC-DB                                                                R  0065
      IS=2                                                                      R  0067
      GO TO 3                                                                   R  0068
    6 DA=DB                                                                     R  0069
```

```
      FA=FB                                                             R  0071
      FB=FC                                                             R  0072
   32 DC=X                                                              R  0074
      FC=F                                                              R  0075
      GO TO 14                                                          R  0076
    5 IF(FB-FC)16,17,17                                                 R  0077
   17 IF(F-FB)18,32,32                                                  R  0081
   18 FA=FB                                                             R  0084
      DA=DB                                                             R  0085
   19 FB=F                                                              R  0087
      DB=X                                                              R  0088
      GO TO 14                                                          R  0089
   16 IF(FA-FC)21,21,20                                                 R  0090
   20 XINC=FA                                                           R  0094
      FA=FC                                                             R  0095
      FC=XINC                                                           R  0096
      XINC=DA                                                           R  0097
      DA=DC                                                             R  0099
      DC=XINC                                                           R  0100
   21 XINC=DC                                                           R  0102
      IF((D-DB)*(D-DC))32,22,22                                         R  0103
   22 IF(F-FA)23,24,24                                                  R  0106
   23 FC=FB                                                             R  0111
      DC=DB                                                             R  0112
      GO TO 19                                                          R  0113
   24 FA=F                                                              R  0114
      DA=X                                                              R  0115
   14 IF(FB-FC)25,25,29                                                 R  0116
   25 IINC=2                                                            R  0120
      XINC=DC                                                           R  0121
      IF(FB-FC)29,45,29                                                 R  0122
   29 D=(FA-FB)/(DA-DB)-(FA-FC)/(DA-DC)                                 R  0126
      IF(D*(DB-DC))33,33,37                                             R  0132
   37 D=0.5*(DB+DC-(FB-FC)/D)                                           R  0137
      IF(ABS(D-X)-ABS(ABSACC))34,34,35                                  R  0143
   35 IF(ABS(D-X)-ABS(D*RELACC))34,34,36                                R  0146
   34 ITEST=2                                                           R  0153
      GO TO 43                                                          R  0153
   36 IS=1                                                              R  0155
      X=D                                                               R  0156
      IF((DA-DC)*(DC-D))3,26,38                                         R  0157
```

```
   38 IS=2
      GO TO (39,40),IINC
   39 IF(ABS(XINC)-ABS(DC-D))41,3,3
   33 IS=2
      GO TO (41,42),IINC
   41 X=DC
      GO TO 10
   40 IF(ABS(XINC-X)-ABS(X-DC))42,42,3
   42 X=0.5*(XINC+DC)
      IF((XINC-X)*(X-DC))26,26,3
   45 X=0.5*(DB+DC)
      IF((DB-X)*(X-DC))26,26,3
   26 ITEST=3
      GO TO 43
      END
```

```
                                    R  0164
                                    R  0165
                                    R  0171
                                    R  0176
                                    R  0177
                                    R  0183
                                    R  0184
                                    R  0185
                                    R  0190
                                    R  0194
                                    R  0198
                                    R  0202
                                    R  0206
                                    R  0206
                                    R  0207
                        SEGMENT     8 IS   220 LONG

                        SEGMENT     9 IS    17 LONG
                        SEGMENT    10 IS    29 LONG
                        SEGMENT    11 IS   138 LONG
              START OF SEGMENT ********** 12
                        SEGMENT    12 IS    15 LONG
```


NUMBER OF CARDS = 554

COMPILATION TIME = 29 SECS;

CORE MEMORY ALLOCATION = 6400 WORDS.

ELAPSED TIME = 67 SECS

Table J.1 Parameter estimation for system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$ and H_2SO_4.

NO OF COMPONENTS = 3 NO OF REACTIONS = 2

NO OF DATA SETS = 22 NO OF PARAMETERS = 2
20 1000 .100E 03

TOLERANCE ON PARAMETERS
.10000E-03 .10000E-03

INITIAL GUESSES
.0 .0

INDEX	RESIN SPECIES
1	SO_4
2	HSO_4
3	NO_3

REACTION(I)

	COMPONENT 1	2	3
1	-1.00	2.00	0.00
2	-1.00	0.00	2.00

EXP NUMBER	EQU RATIO λ	MOLE FRACTION ON RESIN, x_j		
		COMPONENT 1	2	3
111011	.26780E 01	.16419E 00	.54995E 00	.28587E 00
111012	.23520E 01	.12849E 00	.44588E 00	.42563E 00
111013	.21870E 01	.75550E-01	.30143E 00	.62302E 00
111014	.22240E 01	.41470E-01	.21172E 00	.74681E 00
111015	.20963E 01	.26480E-01	.14752E 00	.82601E 00
111016	.17100E 01	.25070E-01	.10877E 00	.86616E 00
112011	.76590E 01	.31440E 00	.19780E 00	.48780E 00
112012	.52530E 01	.21903E 00	.12684E 00	.65413E 00
112013	.32930E 01	.10648E 00	.65370E-01	.82615E 00
112014	.24340E 01	.55080E-01	.33020E-01	.91190E 00
112015	.20970E 01	.22370E-01	.15210E-01	.96240E 00
111021	.40393E 02	.16419E 00	.54995E 00	.28587E 00
111022	.26403E 02	.12849E 00	.44588E 00	.42563E 00

111024	•19443E 02	•41470E-01	•21172E 00	•74681E 00
111025	•16415E 02	•26480E-01	•14752E 00	•82601E 00
111026	•12550E 02	•25070E-01	•10877E 00	•86616E 00
112021	•75106E 02	•31440E 00	•19780E 00	•48780E 00
112022	•43443E 02	•21903E 00	•12684E 00	•65413E 00
112023	•26776E 02	•10848E 00	•65370E-01	•82615E 00
112024	•19680E 02	•55080E-01	•33020E-01	•91190E 00
112025	•17560E 02	•22370E-01	•15210E-01	•96240E 00

ITERATION 0 3 CALLS OF CALFUN F= •15908842992500E 01

VARIABLES

•0 •0

FUNCTIONS

•11705072852600E 00	•14824389582800E 00	•30882442532700E 00	•44791662082400E 00	•46695958458800E 00
•35046430916600E 00	•31479940440700E 00	•32959706073200E 00	•40124236658300E 00	•42220462166600E 00
•46844440722500E 00	•20026409066100E 00	-•41845137701100E-01	-•35078743892400E-01	•10869482369500E 00
•35069456519300E-01	-•25903921612400E 00	•12463055854600E 00	-•55167843908000E-01	-•58989289331000E-02
•85856983669000E-03	•10007654102200E 00			

VA02A FINAL VALUES OF FUNCTIONS AND VARIABLES

ITERATION 7 43 CALLS OF CALFUN F= •28315044728000E 00

VARIABLES

•98997276098000E 00 -•12845266791000E 01

FUNCTIONS

-•70154793635000E-01	-•96658662490000E-01	•48426759955600E-01	•20955568623000E 00	•20242047078000E 00
-•98836695746000E-02	-•76544210420000E-02	-•79111131175000E-01	-•17656172238700E-01	•85634793751000E-02
•91152498950000E-01	-•12254563502000E 00	-•23636499173900E 00	-•49553651421300E-01	•14063028540700E 00
•74459083391000E-01	-•21755984874800E 00	•28427907567200E-01	-•99504863229000E-01	-•66507724131000E-02
•74796719518000E-02	•10499142958600E 00			

EXP NUM	EQ RATIO EXP	EQ RATIO CALC	FRACTION RESIN COMPONENT			ACT COEFF CALC COMPONENT		
			1	2	3	1	2	3
111011	.26780E 01	.28659E 01	.16419E 00	.54995E 00	.28587E 00	.41613E 00	.86037E 00	.81816E 00
111012	.23520E 01	.25793E 01	.12849E 00	.44588E 00	.42563E 00	.35927E 00	.84267E 00	.89560E 00
111013	.21870E 01	.20811E 01	.75550E-01	.30143E 00	.62302E 00	.27351E 00	.81855E 00	.96535E 00
111014	.22240E 01	.17579E 01	.41470E-01	.21172E 00	.74681E 00	.22371E 00	.80545E 00	.98821E 00
111015	.20963E 01	.16720E 01	.26480E-01	.14752E 00	.82601E 00	.20630E 00	.79312E 00	.99521E 00
111016	.17160E 01	.17330E 01	.25070E-01	.10877E 00	.86616E 00	.20822E 00	.78264E 00	.99695E 00
112011	.76590E 01	.77176E 01	.31440E 00	.19780E 00	.48780E 00	.65574E 00	.65815E 00	.80960E 00
112012	.52530E 01	.56606E 01	.21903E 00	.12684E 00	.65413E 00	.52038E 00	.68411E 00	.89142E 00
112013	.32930E 01	.33511E 01	.10848E 00	.65370E-01	.82615E 00	.34560E 00	.72509E 00	.96703E 00
112014	.24340E 01	.24132E 01	.55080E-01	.33020E-01	.91190E 00	.26276E 00	.74506E 00	.99056E 00
112015	.20970E 01	.19059E 01	.22370E-01	.15210E-01	.96240E 00	.21477E 00	.75795E 00	.99837E 00
111021	.40393E 02	.45343E 02	.16419E 00	.54995E 00	.28587E 00	.41613E 00	.86037E 00	.81816E 00
111022	.26483E 02	.32670E 02	.12849E 00	.44588E 00	.42563E 00	.35927E 00	.84267E 00	.89560E 00
111023	.20397E 02	.21408E 02	.75550E-01	.30143E 00	.62302E 00	.27351E 00	.81855E 00	.96535E 00
111024	.19443E 02	.16709E 02	.41470E-01	.21172E 00	.74681E 00	.22371E 00	.80545E 00	.98821E 00
111025	.16415E 02	.15193E 02	.26480E-01	.14752E 00	.82601E 00	.20630E 00	.79312E 00	.99521E 00
111026	.12550E 02	.15280E 02	.25070E-01	.10877E 00	.86616E 00	.20822E 00	.78264E 00	.99695E 00
112021	.75106E 02	.72971E 02	.31440E 00	.19780E 00	.48780E 00	.65574E 00	.65815E 00	.80960E 00
112022	.43443E 02	.47766E 02	.21903E 00	.12684E 00	.65413E 00	.52038E 00	.68411E 00	.89142E 00
112023	.26778E 02	.26956E 02	.10848E 00	.65370E-01	.82615E 00	.34560E 00	.72509E 00	.96703E 00
112024	.19680E 02	.19533E 02	.55080E-01	.33020E-01	.91190E 00	.26276E 00	.74506E 00	.99056E 00
112025	.17560E 02	.15716E 02	.22370E-01	.15210E-01	.96240E 00	.21477E 00	.75795E 00	.99837E 00

REACTION NO	THERMODYNAMIC CONSTANT
1	.50980E 01
2	.72939E 02

PARAMETERS - LAMDA(I,J)

COMPONENT	1	2	3
1	.10000E 01	.98460E 00	.65419E 00
2	.28124E 01	.10000E 01	.26912E 01
3	.15287E 01	.37137E 00	.10000E 01

```
FILE  2 =  INPUT              ,UNIT = READER                                  R  0000
FILE  3 =  OUTPUT             ,UNIT = PRINTER                                 R  0000
C---------- NOPTION = 1 SOLUTION EXTENTS ONLY                                 R  0000
C----------NOPTION = 2 RESIN EXTENTS ONLY                                     R  0000
C---------- NOPTION = 3 SOLUTION AND RESIN EXTENTS                            R  0000
C--------M          NO OF DATA SETS                                           R  0000
C--------N          NO OF PARAMETERS                                          R  0000
C--------CT(I)      EQUILIBRIUM CONSTANTS                                     R  0000
C--------E(I)       TOLERANCE FOR EXTENTS                                     R  0000
C--------X(I)       EXTENTS OF REACTION (MOLES OR MOLES PER LITRE)            R  0000
C--------S          NUMBER OF SOLUTION SPECIES                                R  0000
C--------CONCOJ     INITIAL CONCENTRATION IN SOLUTION (MOLES PER LITRE)       R  0000
C--------ALPHA      STOICHIOMETRIC COEFFICIENTS, + PRODUCTS - REACTANTS       R  0000
C--------Z          CHARGE OF SOLUTION SPECIES                                R  0000
C--------DRB        DEBYE-HUCKEL PARAMETER OF ION                             R  0000
C--------DBA        DEBYE-HUCKEL PARAMETER OF ION                             R  0000
C--------DHA,DHB    TEMPERATURE DEPENDENT PARAMETERS                          R  0000
C--------VSLO       VOLUME OF SOLUTION                                        R  0000
C--------MU         IONIC STRENGTH                                            R  0000
C--------CNS        CONCENTRATION OF SPECIES IN SOLUTION (MOLES PER LITRE)    R  0000
C--------SGAM       ACTIVITY COEFFICIENT IN SOLUTION                          R  0000
C--------SACTIV     ACTIVITY OF SPECIES IN SOLUTION                           R  0000
C--------P          NUMBER OF RESIN SPECIES                                   R  0000
C--------KRES       NUMBER OF RESIN REACTIONS                                 R  0000
C--------CONCOK     INITIAL MOLES OF SPECIES K IN RESIN                       R  0000
C--------BETA       STOICHIOMETRIC COEFFICIENTS OF RESIN SPECIES              R  0000
C--------B          WILSON PARAMETERS                                         R  0000
C--------VFSR       VOLUME OF FREE SETTLED RESIN IN SULPHATE FORM             R  0000
C--------CAP        CAPACITY OF RESIN  (EQUIV. PER LITRE FSR)                 R  0000
C--------CNR        MOLES OF RESIN SPECIES                                    R  0000
C--------FRAC       MOLE FRACTION OF RESIN SPECIES                            R  0000
C--------RGAM       ACTIVITY COEFFICIENT OF RESIN SPECIES                     R  0000
C--------RACTIV     ACTIVITY OF RESIN SPECIES                                 R  0000
C--------NSYS       NO OF SYSTEMS                                             R  0000
C--------RZ         IONIC OF RESIN SPECIES                                    R  0000
C--------EQFR       EQUIVALENT FRACTION ON RESIN                              R  0000
```

```
                                                                START OF SEGMENT **********    1
      DOUBLE PRECISION F,W,X,E,DHA,DHB,CT,CONCOJ,CNS,SGAM,CNSJ,SGNSJ,                    R  0000
     1DBA,DBB,MU,MUHALF,SMU,ESCALE,CONCOK,CNR,CNPK,RCNRK,R,VSLO,VFSR,CAP                R  0000
     S,ERSUM,ERAC,GAM,XSUM,XSUM1,XSUM2,SACTIV,RACTIV,ANCAT,TERM,Z,RZ                    R  0000
      DOUBLE PRECISION EPS,H                                                            R  0000
      COMMON/A/DHA,DHB,S,KOUNT,P,KRES                                                   R  0000
      COMMON/B/CT(20),ALPHA(30,30),BETA(30,30)                                          R  0000
      COMMON/I/NOPTION                                                                  R  0000
      DIMENSION F(20),X(20),W(400),E(20)                                                R  0000
      DIMENSION H(1)                                                                    R  0000
      COMMON/H/SACTIV(30),RACTIV(30)                                                    R  0000
      INTEGER S,P,NAME(10)                                                              R  0000
      READ(2,101)IPRINT                                                                 R  0000
      WRITE(3,101)IPRINT                                                                R  0009
  101 FORMAT(I3)                                                                        R  0020
      READ(2,200)ESCALE                                                                 R  0020
      WRITE(3,200)ESCALE                                                                R  0029
      READ(2,102)MAXFUN                                                                 R  0039
      READ(2,102)NOPTION                                                                R  0049
      READ(2,100)M,N                                                                    R  0060
      READ(2,102)NSYS                                                                   R  0072
  100 FORMAT(5I5)                                                                       R  0083
  102 FORMAT(I5)                                                                        R  0083
      READ(2,200)(CT(I),I=1,N)                                                          R  0083
      READ(2,200)(E(I),I=1,N)                                                           R  0103
      IF(NOPTION.NE.2)READ(2,200)(X(I),I=1,N)                                           R  0121
  200 FORMAT(4D20.13)                                                                   R  0141
      WRITE(3,1000)N                                                                    R  0141
 1000 FORMAT(//5X,"NUMBER OF REACTIONS =",I5)                                           R  0151
      WRITE(3,1001)                                                                     R  0151
 1001 FORMAT(//5X,12HREACTION NO.,5X,20HEQUILIBRIUM CONSTANT)                           R  0155
      DO 5 I=1,N                                                                        R  0155
      WRITE(3,1002)I,CT(I)                                                              R  0160
 1002 FORMAT(10X,I5,10X,D20.13)                                                         R  0177
    5 CONTINUE                                                                          R  0177
      WRITE(3,1003)                                                                     R  0177
 1003 FORMAT(//5X,12HREACTION NO.,5X,14HTOL. ON EXTENT)                                 R  0181
      DO 6 I=1,N                                                                        R  0181
      WRITE(3,1004)I,E(I)                                                               R  0186
 1004 FORMAT(10X,I5,10X,D20.13)                                                         R  0201
    6 CONTINUE                                                                          R  0201
      GO TO(10,20,30),NOPTION                                                           R  0201
   10 CALL SOLIN1(5)                                                                    R  0208
```

```
      CALL CHECK                                                        R  0208
      EPS = E(1)                                                        R  0209
      H(1) = 0.01*X(1)                                                  R  0212
      IF(N.EQ.1)CALL NELM(X,F,EPS,H)                                    R  0222
      IF(N.EQ.1)WRITE(3,1005)X(1),F(1)                                  R  0228
1005  FORMAT(//5X,"EXTENT=",D20.13,5X,"F VALUE=",D20.13)                R  0244
      IF(N.EQ.1)GO TO 21                                                R  0244
      CALL VA02A(M,N,F,X,E,ESCALE,IPRINT,MAXFUN)                        R  0246
21    CALL SOLOUT1                                                      R  0252
      GO TO 40                                                          R  0252
20    CALL SOLIN2(N)                                                    R  0254
      CALL RESIN(N)                                                     R  0254
      DO 80 II=1,NSYS                                                   R  0255
      READ(2,200)(SACTIV(J),J=1,S)                                      R  0260
      READ(2,200)(X(IJ),IJ=1,N)                                         R  0279
      WRITE(3,7000)                                                     R  0297
7000  FORMAT(//2X,"ACTIVITY OF SPECIES J IN SOLUTION")                  R  0301
      WRITE(3,1114)(SACTIV(J),J=1,S)                                    R  0301
1114  FORMAT(/5X,5D20.13)                                               R  0320
       WRITE(3,3000)                                                    R  0320
3000   FORMAT(//5X,12HREACTION NO.,5X,24HINITIAL GUESS FOR EXTENT)      R  0324
      DO 60 IIJ = 1,N                                                   R  0324
      WRITE(3,3001)IIJ,X(IIJ)                                           R  0329
3001   FORMAT(10X,I5,10X,D20.13)                                        R  0344
60    CONTINUE                                                          R  0344
      EPS = E(1)                                                        R  0344
      H(1) = 0.01*X(1)                                                  R  0347
      IF(N.EQ.1)CALL NELM(X,F,EPS,H)                                    R  0357
      IF(N.EQ.1)WRITE(3,1005)X(1),F(1)                                  R  0363
      IF(N.EQ.1)GO TO 22                                                R  0378
      CALL VA02A(M,N,F,X,E,ESCALE,IPRINT,MAXFUN)                        R  0380
22    CALL RESOUT                                                       R  0386
80    CONTINUE                                                          R  0387
      GO TO 40                                                          R  0387
30    CALL SOLIN1(N)                                                    R  0389
      CALL CHECK                                                        R  0389
      CALL RESIN(N)                                                     R  0390
      CALL VA02A(M,N,F,X,E,ESCALE,IPRINT,MAXFUN)                        R  0391
      CALL SOLOUT1                                                      R  0396
      CALL RESOUT                                                       R  0396
40    STOP                                                              R  0397
      END                                                               R  0398

                                SEGMENT    1 IS   415 LONG
```

```
                                                                  START OF SEGMENT **********    2
      SUBROUTINE CHECK                                                                R  0000
      DOUBLE PRECISION F,W,X,E,DHA,DHB,CT,CONCOJ,CNS,SGAM,CNSJ,SGNSJ,                 R  0000
     1DBA,DBB,MU,MUHALF,SMU,ESCALE,CONCOK,CNR,CNRK,RGNRK,B,VSLO,VFSR,CAP              R  0000
     $,FRSUM,FRAC,PGAM,XSLUM,XSUM1,XSUM2,SACTIV,PACTIV,ANCAT,TERM,Z,RZ               R  0000
      COMMON/A/DHA,DHB,S,KOUNT,P,KRES                                                 R  0000
      COMMON/C/CONCOJ(30),CNS(30),CONCOK(30),CNR(30),RGAM(30)                         R  0000
      COMMON/E/SGAM(30),DBA(30),DBB(30),MU     ,Z(30)                                 R  0000
      INTEGER S,P,NAME(10)                                                            R  0000
C-----CHECK CATION ANION BALANCE                                                      R  0000
      ANCAT = 0.0                                                                     R  0000
      DO 90 J=1,S                                                                     R  0001
      ANCAT = ANCAT + CONCOJ(J)*Z(J)                                                  R  0007
 90   CONTINUE                                                                        R  0017
      IF(DABS(ANCAT).LT.0.001)GO TO 92                                                R  0017
      WRITE(3,9001)                                                                   R  0023
 9001 FORMAT(//2X,"NO CATION-ANION BALANCE")                                          R  0027
      STOP                                                                            R  0027
 92   RETURN                                                                          R  0029
      END                                                                             R  0032
                                                                  SEGMENT    2 IS    37 LONG
```

```
                                                                  START OF SEGMENT **********    3
      SUBROUTINE SOLIN1(N)                                                            R  0000
      DOUBLE PRECISION F,W,X,E,DHA,DHB,CT,CONCOJ,CNS,SGAM,CNSJ,SGNSJ,                 R  0000
     1DBA,DBB,MU,MUHALF,SMU,ESCALE,CONCOK,CNR,CNRK,RGNRK,B,VSLO,VFSR,CAP              R  0000
     $,FRSUM,FRAC,PGAM,XSLUM,XSUM1,XSUM2,SACTIV,PACTIV,ANCAT,TERM,Z,RZ               R  0000
      COMMON/A/DHA,DHB,S,KOUNT,P,KRES                                                 R  0000
      COMMON/B/CT(20),ALPHA(30,30),BETA(30,30)                                        R  0000
      COMMON/C/CONCOJ(30),CNS(30),CONCOK(30),CNR(30),RGAM(30)                         R  0000
      COMMON/D/CNSJ(30),SGNSJ(30),CNRK(30),RGNRK(30),B(30,30)                         R  0000
      COMMON/E/SGAM(30),DBA(30),DBB(30),MU     ,Z(30)                                 R  0000
      COMMON/G/VSLO,VFSR,CAP                                                          R  0000
      INTEGER S,P,NAME(10)                                                            R  0000
```

```
      READ(2,102)S                                                      R  0000
      WRITE(3,5000)                                                     R  0010
 5000 FORMAT(//2X,"INDEX",2X,"SOLUTION SPECIES")                        R  0014
      DO 50 J=1,S                                                       R  0014
      READ(2,5001)J,NAME                                                R  0020
      WRITE(3,5002)J,NAME                                               R  0035
 5001 FORMAT(I3,10A1)                                                   R  0051
 5002 FORMAT(/2X,I3,5X,10A1)                                            R  0051
 50   CONTINUE                                                          R  0051
      READ(2,200)(CONCO.J(J),J=1,S)                                     R  0051
      DO 7 I=1,N                                                        R  0070
      READ(2,400)(ALPHA(I,J),J=1,S)                                     R  0075

 4    CONTINUE                                                          R  0098
      READ(2,400)(Z(J),J=1,S)                                           R  0098
      READ(2,200)(DBA(J),J=1,S)                                         R  0117
      READ(2,200)(DBB(J),J=1,S)                                         R  0135
      READ(2,900)DHA,DHB                                                R  0153
      READ(2,103)VSLO                                                   R  0166
 102  FORMAT(I5)                                                        R  0178
 103  FORMAT(3D20.13)                                                   R  0178
 200  FORMAT(4D20.13)                                                   R  0178
 400  FORMAT(10F5.2)                                                    R  0178
 900  FORMAT(2D20.13)                                                   R  0178
      WRITE(3,1000)S                                                    R  0178
 1000 FORMAT(//5X,"NUMBER OF SOLUTION SPECIES = ",I5)                   R  0189

                                                  SEGMENT    4 IS   122 LONG
       WRITE(3,1109)                                                    R  0189
 1109  FORMAT(//2X,34HINITIAL CONCENTRATION OF SPECIES J)               R  0193
      WRITE(3,1009)(CONCO.J(J),J=1,S)                                   R  0193
 1009  FORMAT(/5X,5D20.13)                                              R  0212
      WRITE(3,1005)                                                     R  0212
 1005 FORMAT(//50X,10HSPECIES(J))                                       R  0216
      WRITE(3,1006)                                                     R  0216
 1006 FORMAT(2X,11HREACTION(I))                                         R  0220
      WRITE(3,1007)(J,J=1,S)                                            R  0220
 1007 FORMAT(13X,10I5)                                                  R  0237
      DO 7 I=1,N                                                        R  0237
      WRITE(3,1008)I,(ALPHA(I,J),J=1,S)                                 R  0242
 1008 FORMAT(5X,I5,5X,10F5.2)                                           R  0267
 7    CONTINUE                                                          R  0267
```

```
      WRITE(3,1110)                                                    R  0267
1110  FORMAT(//2X,25HIONIC CHARGE OF SPECIES J)                        R  0271
      WRITE(3,1010)(Z(J),J=1,S)                                        R  0271
1010  FORMAT(/5X,10F5.2)                                               R  0290
      WRITE(3,1011)                                                    R  0290
1011  FORMAT(//2X,37HDEBYE-HUCKEL PARAMETER A OF SPECIES J)            R  0294
      WRITE(3,1009)(DBA(J),J=1,S)                                      R  0294
      WRITE(3,1012)                                                    R  0312
1012  FORMAT(//2X,37HDEBYE-HUCKEL PARAMETER B OF SPECIES J)            R  0316
      WRITE(3,1009)(DBB(J),J=1,S)                                      R  0316
      WRITE(3,1113)                                                    R  0334
1113  FORMAT(//2X,30HDEBYE-HUCKEL PARAMETER A AND B)                   R  0338
      WRITE(3,1013)DHA,DHB                                             R  0338
1013  FORMAT(/5X,2D20.13)                                              R  0352
      WRITE(3,1022)VSLO                                                R  0352
1022  FORMAT(//2X,"VOLUME OF SOLUTION = ",D20.13)                      R  0363
      RETURN                                                           R  0363
      END                                                              R  0366
                                                  SEGMENT    3 IS   375 LONG
```

```
                                                  START OF SEGMENT **********    5
      SUBROUTINE SOLIN2(N)                                             R  0000
      DOUBLE PRECISION F,W,X,E,DHA,DHB,CT,CONCOJ,CNS,SCAM,CNSJ,SGNSJ,  R  0000
     1DBA,DBB,XU,MUHALF,SMU,ESCALE,CONCOK,CNR,CNRK,RGNRK,R,VSLO,VFSR,CAP R  0000
     $,FRSUM,FRAC,RGAM,XSLUM,XSUM1,XSUM2,SACTIV,RACTIV,ANCAT,TERM,Z,RZ R  0000
      COMMON/A/DHA,DHB,S,KOUNT,P,KRES                                  R  0000
      COMMON/B/CT(20),ALPHA(30,30),BETA(30,30)                         R  0000
      COMMON/G/VSLO,VFSR,CAP                                           R  0000
```

```
      COMMON/H/SACTIV(30),RACTIV(30),EQFS(30),FQFR(30),RZ(30)                R  0000
      INTEGER S,P,NAME(10)                                                   R  0000
      READ(2,102)S                                                           R  0000
      WRITE(3,5000)                                                          R  0010
5000  FORMAT(//2X,"INDEX",2X,"SOLUTION SPECIES")                             R  0014
      DO 50 J=1,S                                                            R  0014
      READ(2,5001)J,NAME                                                     R  0020
      WRITE(3,5002)J,NAME                                                    R  0035
5001  FORMAT(I3,10A1)                                                        R  0051
5002  FORMAT(/2X,I3,5X,10A1)                                                 R  0051
50    CONTINUE                                                               R  0051
      DO 4 I=1,N                                                             R  0051
      READ(2,400)(ALPHA(I,J),J=1,5)                                          R  0056
4     CONTINUE                                                               R  0079
      WRITE(3,1005)                                                          R  0079
1005  FORMAT(//5X,"SPECIES(J)")                                              R  0083
      WRITE(3,1006)                                                          R  0083
1006  FORMAT(2X,"REACTION(I)")                                               R  0087
      WRITE(3,1007)(J,J=1,S)                                                 R  0087
1007  FORMAT(13X,10I5)                                                       R  0104
      DO 7 I=1,N                                                             R  0104
      WRITE(3,1008)I,(ALPHA(I,J),J=1,S)                                      R  0109
1008  FORMAT(5X,I5,5X,10F5.2)                                                R  0134
7     CONTINUE                                                               R  0134
102   FORMAT(I5)                                                             R  0135
200   FORMAT(4D20.13)                                                        R  0135

                                                                    SEGMENT    6 IS   125 LONG
400   FORMAT(10F5.2)                                                         R  0135
      RETURN                                                                 R  0135
      END                                                                    R  0138
                                                                    SEGMENT    5 IS   147 LONG
```

```
                                                                  START OF SEGMENT **********    7
      SUBROUTINE RESIN(N)                                                                    R  0000
      DOUBLE PRECISION F,W,X,E,DHA,DHB,CT,CONCOJ,CNS,SGAM,CNSJ,SGNSJ,                        R  0000
     1DBA,DRB,MU,NUHALF,SMU,ESCALE,CONCOK,CNR,CNRK,RGNRK,B,VSLD,VFSR,CAP                     R  0000
     $,FRSUM,FRAC,RGAM,XSUM,XSUM1,XSUM2,SACTIV,RACTIV,ANCAT,TERM,Z,RZ                        R  0000
      COMMON/A/DHA,DHB,S,KOUNT,P,KRES                                                        R  0000
      COMMON/B/CT(20),ALPHA(30,30),BETA(30,30)                                               R  0000
      COMMON/C/CONCOJ(30),CNS(30),CONCOK(30),CNR(30),RGAM(30)                                R  0000
      COMMON/D/CNSJ(30),SGNSJ(30),CNRK(30),RGNRK(30),B(30,30)                                R  0000
      COMMON/G/VSLD,VFSR,CAP                                                                 R  0000
      COMMON/H/SACTIV(30),RACTIV(30),EQFS(30),EQFR(30),RZ(30)                                R  0000
      INTEGER S,P,NAME(10)                                                                   R  0000
      READ(2,102)P                                                                           R  0000
      WRITE(3,5003)                                                                          R  0010
5003  FORMAT(///2X,"INDEX",2Y,"RESIN SPECIES")                                               R  0014
      DO 51 K=1,P                                                                            R  0014
      READ(2,5001)K,NAME                                                                     R  0020
      WRITE(3,5002)K,NAME                                                                    R  0035
51    CONTINUE                                                                               R  0051
      READ(2,400)(RZ(K),K=1,P)                                                               R  0051
      WRITE(3,1110)                                                                          R  0070
1110  FORMAT(//2X,"IONIC CHARGE OF SPECIES J")                                               R  0074
      WRITE(3,1010)(PZ(K),K=1,P)                                                             R  0074
1010  FORMAT(/5X,10F5.2)                                                                     R  0093
5001  FORMAT(I3,10A1)                                                                        R  0093
5002  FORMAT(/2X,I3,5X,10A1)                                                                 R  0093
      READ(2,102)KRES                                                                        R  0103
      READ(2,200)(CONCOK(K),K=1,P)                                                           R  0122
      DO 20 I=1,N                                                                            R  0127
      READ(2,400)(BETA(I,K),K=1,P)                                                           R  0150
20    CONTINUE                                                                               R  0150
      DO 40 K=1,P                                                                            R  0156
      READ(2,200)(B(K,L),L=1,P)                                                              R  0179
40    CONTINUE                                                                               R  0179
      READ(2,103)VFSR,CAP                                                                    R  0194
103   FORMAT(3020.13)                                                                        R  0194
102   FORMAT(I5)                                                                             R  0194
200   FORMAT(4020.13)                                                                        R  0194
400   FORMAT(10F5.2)                                                                         R  0194
      WRITE(3,1000)P,KRES                                                                    R  0194
1000  FORMAT(//5X,"NUMBER OF RESIN SPECIES =",I5,//5X,"NUMBER OF RESIN R                     R  0208
```

```
      $EACTIONS = ",15)                                                  R  0208
        WRITE(3,1019)                                                    R  0208
1019    FORMAT(//2X,"INITIAL MOLES OF SPECIES K IN RESIN")               R  0212
        WRITE(3,1009)(CONCOK(K),K=1,P)                                   R  0212
1009  FORMAT(/5X,5D20.13)                                                R  0231
      WRITE(3,1015)                                                      R  0231
1015  FORMAT(//50X,10HSPECIES(K))                                        R  0235
      WRITE(3,1016)                                                      R  0235
1016  FORMAT(2X,11HREACTION(I))                                          R  0239
      WRITE(3,1017)(K,K=1,P)                                             R  0239
1017  FORMAT(13X,10I5)                                                   R  0256
      DO 21 I=1,N                                                        R  0256
      WRITE(3,1018)I,(BETA(I,K),K=1,P)                                   R  0261
1018  FORMAT(5X,I5,5X,10F5.2)                                            R  0286
21    CONTINUE                                                           R  0286
        WRITE(3,1020)                                                    R  0286
1020    FORMAT(//2X,"WILSON INTERACTION PARAMETERS FOR RESIN PHASE")     R  0290
      WRITE(3,1015)                                                      R  0290
      WRITE(3,4000)(K,K=1,P)                                             R  0293
4000  FORMAT(10X,10I10)                                                  R  0311
      DO 41 K=1,P                                                        R  0311
      WRITE(3,4001)K,(B(K,L),L=1,P)                                      R  0317
4001  FORMAT(5X,I5,5X,10D10.5)                                           R  0342
41    CONTINUE                                                           R  0342
      WRITE(3,1023)VFSR,CAP                                              R  0342
1023  FORMAT(//2X,"VOLUME OF FREE SETTLED RESIN IN SULPHATE FORM =",D20.1R  0357
     $3,//2X,"CAPACITY OF RESIN EQUIV. PER LITRE FSR =",D20.13)          R  0357
                                                                 SEGMENT     8 IS   109 LONG
      RETURN                                                             R  0357
      END                                                                R  0360
                                                                 SEGMENT     7 IS   369 LONG


                                                        START OF SEGMENT **********    9
      SUBROUTINE SULOUT1                                                 R  0000
      DOUBLE PRECISION F,W,X,E,DHA,DHB,CT,CONCOJ,CNS,SGAM,CNSJ,SGNSJ,    R  0000
     1DBA,DRB,HU,HUHALF,SHU,ESCALE,CONCOK,CNR,CNRK,RGNRK,B,VSLU,VFSR,CAP R  0000
     $,FRSUM,FRAC,RGAM,XSLUM,XSUM1,XSUM2,SACTIV,RACTIV,ANCAT,TERM,Z,RZ   R  0000
      COMMON/A/DHA,DHB,S,KOUNT,P,KRES                                    R  0000
      COMMON/C/CONCOJ(30),CNS(30),CONCOK(30),CNR(30),RGAM(30)            R  0000
```

```
      COMMON/E/SGAM(30),DBA(30),DBB(30),MU     ,Z(30)                          R  0000
      COMMON/P/SACTIV(30),RACTIV(30),EQFS(30),EQFP(30),RZ(30)                  R  0000
      INTEGER S,P,NAME(10)                                                     R  0000
      WRITE(3,6000)MU                                                          R  0000
 6000 FORMAT(//2X,"IONIC STRENGTH OF SOLUTION = ",D20.13)                      R  0011
       WRITE(3,803)                                                           R  0011
  803  FORMAT(//2X,66HEQUILIBRIUM CONCENTRATION OF SPECIES J IN MOLES PE      R  0015
     $R LITRE SOLUTION)                                                      R  0015
       WRITE(3,1114)(CNS(J),J=1,S)                                            R  0015
      SUM= 0.0                                                               R  0033
      DO 90 J=1,S                                                            R  0034
      SUM = SUM+DABS(Z(J))*CNS(J)                                            R  0040
  90  CONTINUE                                                               R  0051
      DO 91 J=1,S                                                            R  0051
      EQFS(J) = DABS(Z(J))*CNS(J)/(0.5*SUM)                                  R  0057
  91  CONTINUE                                                               R  0071
      WRITE(3,804)                                                           R  0071
  804 FORMAT(//2X,"EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES J IN SOLUT     R  0075
     $ION")                                                                  R  0075
      WRITE(3,1114)(EQFS(J),J=1,S)                                           R  0075
       WRITE(3,900)                                                          R  0092
  800  FORMAT(//2X,34HACTIVITY COEFFICIENTS OF SPECIES J)                    R  0096
       WRITE(3,1114)(SGAM(J),J=1,S)                                          R  0096
 1114 FORMAT(/5X,5D20.13)                                                    R  0115
      DO 70 J=1,S                                                            R  0115
      SACTIV(J) = CNS(J)*SGAM(J)                                             R  0121
  70  CONTINUE                                                               R  0134
      WRITE(3,7000)                                                          R  0134
 7000 FORMAT(//2X,"ACTIVITY OF SPECIES J IN SOLUTION")                       R  0138
      WRITE(3,1114)(SACTIV(J),J=1,S)                                         R  0138
      RETURN                                                                 R  0156
      END                                                                    R  0159

                                                SEGMENT    9 IS   164 LONG
```

```
                                                                START OF SEGMENT **********  10
      SUBROUTINE RESOUT                                                          R  0000
      DOUBLE PRECISION F,W,X,E,DHA,DHB,CT,CONCOJ,CNS,SGAM,CNSJ,SGNSJ,            R  0000
     1DBA,DBB,MU,MUHALF,SMU,ESCALE,CONCOK,CNR,CNPK,RGNRK,B,VSLD,VFSR,CAP         R  0000
     $,FRSUM,FRAC,RGAM,XSLUM,XSUM1,XSUM2,SACTIV,RACTIV,ANCAT,TERM,Z,RZ           R  0000
      COMMON/A/DHA,DHB,S,KOUNT,P,KRES                                            R  0000
      COMMON/C/CONCOJ(30),CNS(30),CONCOK(30),CNR(30),RGAM(30)                    R  0000
      COMMON/F/FRAC(30)                                                          R  0000
      COMMON/G/VSLD,VFSR,CAP                                                     R  0000
      COMMON/H/SACTIV(30),RACTIV(30),EQFS(30),EQFR(30),RZ(30)                    R  0000
      INTEGER S,P,NAME(10)                                                       R  0000
       WRITE(3,1021)                                                             R  0000
 1021 FORMAT(//2X,"EQUILIBRIUM MOLES OF SPECIES K")                             R  0004
       WRITE(3,1114)(CNR(K),K=1,P)                                               R  0004
       WRITE(3,1014)                                                             R  0022
 1014 FORMAT(//2X,"EQUILIBRIUM MOLE FRACTION OF SPECIES K IN RESIN")            R  0026
      WRITE(3,1114)(FRAC(K),K=1,P)                                              R  0026
      DO 10 K=1,P                                                               R  0044
      EQFR(K) = DABS(RZ(K))*CNR(K)/(VFSR*CAP)                                   R  0050
 10     CONTINUE                                                                R  0063
      WRITE(3,1200)                                                             R  0063
 1200 FORMAT(//2X,"EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES K IN RESIN        R  0067
     $")                                                                        R  0067
      WRITE(3,1114)(EQFR(K),K=1,P)                                              R  0067
       WRITE(3,801)                                                             R  0094
  801  FORMAT(//2X,"ACTIVITY COEFFICIENT OF SPECIES K IN RESIN")                 R  0098
      WRITE(3,1114)(RGAM(K),K=1,P)                                              R  0098
      DO 71 K=1,P                                                               R  0106
      RACTIV(K) = FRAC(K)*RGAM(K)                                               R  0112
  71  CONTINUE                                                                  R  0125
      WRITE(3,7001)                                                             R  0125
 7001 FORMAT(//2X,"ACTIVITY OF SPECIES K IN RESIN")                             R  0129
      WRITE(3,1114)(RACTIV(K),K=1,P)                                            R  0129
 1114 FORMAT(/5X,5020.13)                                                       R  0148
       DO 31 K=1,P                                                              R  0148
      CNR(K)=CNR(K)/VFSR                                                        R  0154
 31    CONTINUE                                                                 R  0164
       WRITE(3,804)                                                             R  0164
  804  FORMAT(//2X,93HEQUILIBRIUM CONCENTRATION OF SPECIES K IN MOLES PE        R  0168
     $R LITRE FREE SETTLED RESIN IN SULPHATE FORM)                              R  0168
                                                        SEGMENT   11 IS  119 LONG
```

```
      WRITE(3,1114)(CNR(K),K=1,P)                                        R  0168
      RETURN                                                             R  0186
      END                                                                R  0189
                                                                SEGMENT    10 IS   193 LONG
```

```
                                                          START OF SEGMENT **********  12
      SUBROUTINE DEBYE                                                   R  0000
      DOUBLE PRECISION F,W,X,E,DHA,DHB,CT,CONCOJ,CNS,SGAM,CNSJ,SGNSJ,    R  0000
     1DBA,DBB,MU,MUHALF,SMU,ESCALE,CONCOK,CNR,CNRK,RGNRK,B,VSLO,VFSR,CAP R  0000
     $,FRSUM,FRAC,RGAM,XSLON,XSUM1,XSUM2,SACTIV,RACTIV,ANCAT,TERM,Z,RZ   R  0000
      COMMON/A/DHA,DHB,S,KOUNT,P,KRES                                    R  0000
      COMMON/C/CONCOJ(30),CNS(30),CONCOK(30),CNR(30),SGAM(30)            R  0000
      COMMON/E/SGAM(30),DBA(30),DBB(30),MU     ,Z(30)                    R  0000
      INTEGER S,P,NAME(10)                                               R  0000
      SMU = 0.0                                                          R  0000
      DO 1 J= 1,S                                                        R  0001
      SMU = SMU + CNS(J)*Z(J)**2.0                                       R  0007
1     CONTINUE                                                           R  0020
      MU = 0.5*SMU                                                       R  0020
      MUHALF = DSQRT(MU)                                                 R  0028
      DO 3 J = 1,S                                                       R  0030
      SGAM(J)=10.0**(-1.0*(DHA*MUHALF*Z(J)**2.0)/(1.0+DHB*DBA(J)*MUHALF) R  0037
     $+DBB(J)*MU)                                                        R  0062
3     CONTINUE                                                           R  0072
      RETURN                                                             R  0072
      END                                                                R  0075
                                                                SEGMENT    12 IS    80 LONG
```

```
                                                                  START OF SEGMENT **********  13
      SUBROUTINE EXCESS                                                                    R  0000


      DOUBLE PRECISION F,W,X,E,DHA,DHB,CT,CONCOJ,CNS,SGAM,CNSJ,SGNSJ,                      R  0000
     1DBA,DBB,MU,MUHALF,SMU,ESCALE,CONCOK,CNR,CNRK,RGNRK,B,VSLO,VFSR,CAP                  R  0000
     $,FRSUM,FRAC,RGAM,XSLUM,XSUM1,XSUM2,SACTIV,RACTIV,ANCAT,TERM,Z,RZ                    R  0000
      COMMON/A/DHA,DHB,S,KOUNT,P,KRES                                                     R  0000
      COMMON/C/CONCOJ(30),CNS(30),CONCOK(30),CNR(30),RGAM(30)                             R  0000
      COMMON/D/CNSJ(30),SGNSJ(30),CNRK(30),RGNRK(30),B(30,30)                             R  0000
      COMMON/F/FRAC(30)                                                                   R  0000
      INTEGER S,P,NAME(10)                                                                R  0000
      DO 100 I=1,P                                                                        R  0000
      XLSUM = 0.0                                                                         R  0006
      XSUM1 = 0.0                                                                         R  0007
      DO 70 J=1,P                                                                         R  0009
      XLSUM = XLSUM + FRAC(J)*B(I,J)                                                      R  0015
      XSUM2 = 0.0                                                                         R  0029
      DO 60 M=1,P                                                                         R  0030
      XSUM2 = XSUM2 + FRAC(M)*B(J,M)                                                      R  0036
60    CONTINUE                                                                            R  0049
      XSUM1 = XSUM1 + FRAC(J)*B(J,I)/XSUM2                                                R  0049
70    CONTINUE                                                                            R  0063
      RGAM(I) = DEXP(1.0-XSUM1)/XLSUM                                                     R  0063
100   CONTINUE                                                                            R  0075
      RETURN                                                                              R  0075
      END                                                                                 R  0078
                                                                  SEGMENT   13 IS    84 LONG
```

```
                                                                  START OF SEGMENT **********  14
      SUBROUTINE CALFUN(M,N,F,X)                                                          R  0000
      DOUBLE PRECISION F,W,X,E,DHA,DHB,CT,CONCOJ,CNS,SGAM,CNSJ,SGNSJ,                     R  0000
     1DBA,DBB,MU,MUHALF,SMU,ESCALE,CONCOK,CNR,CNRK,RGNRK,B,VSLO,VFSR,CAP                  R  0000
     $,FRSUM,FRAC,RGAM,XSLUM,XSUM1,XSUM2,SACTIV,RACTIV,ANCAT,TERM,Z,RZ                    R  0000
      COMMON/A/DHA,DHB,S,KOUNT,P,KRES                                                     R  0000
```

```
      COMMON/B/CT(20),ALPHA(30,30),BETA(30,30)                          R  0000
      COMMON/C/CONCOJ(30),CNS(30),CONCOK(30),CNR(30),RGAM(30)           R  0000
      COMMON/D/CNSJ(30),SGNSJ(30),CNRK(30),RGNRK(30),B(30,30)           R  0000
      COMMON/E/SGAM(30),DBA(30),DBR(30),MU      ,Z(30)                  R  0000
      COMMON/F/FRAC(30)                                                 R  0000
      COMMON/G/VSLU,VFSR,CAP                                            R  0000
      COMMON/H/SACTIV(30),RACTIV(30),EQFS(30),EQFR(30),RZ(30)           R  0000
      COMMON/I/NOPTION                                                  R  0000
      DIMENSION F(20),X(20),W(400),E(20)                                R  0000
      INTEGER S,P,NAME(10)                                              R  0000
      GO TO(90,91,92),NOPTION                                           R  0000
 90   DO 1 J=1,S                                                        R  0007
      CNS(J) = CONCOJ(J)                                                R  0013
C----------EXTENTS IN SOLUTION MOLES PER LITRE                         R  0015
      DO 2 I=1,M                                                        R  0021
      CNS(J) = CNS(J) +ALPHA(I,J)*X(I)                                  R  0027
 2    CONTINUE                                                          R  0047
 1    CONTINUE                                                          R  0048
      CALL DEBYE                                                        R  0048
      DO 3 II=1,M                                                       R  0049
      CNSJ(II) = 1.0                                                    R  0054
      SGNSJ(II) = 1.0                                                   R  0063
      DO 4 J=1,S                                                        R  0072
      CNSJ(II) = CNSJ(II)*CNS(J)**ALPHA(II,J)                           R  0078
      SGNSJ(II) = SGNSJ(II)*SGAM(J)**ALPHA(II,J)                        R  0100
 4    CONTINUE                                                          R  0123
      F(II) = (CT(II)-CNSJ(II)*SGNSJ(II))/CT(II)                        R  0123
 3    CONTINUE                                                          R  0153
      GO TO 50                                                          R  0153
 91   DO 5 K=1,P                                                        R  0155
C----------EXTENTS IN RESIN MOLES                                      R  0155
      CNR(K) = CONCOK(K)                                                R  0161
      DO 6 I=1,M                                                        R  0169
      CNR(K) = CNR(K) + BETA(I,K)*X(I)                                  R  0175
 6    CONTINUE                                                          R  0195
 5    CONTINUE                                                          R  0196
      FRSUM = 0.0                                                       R  0196
      DO 30 K=1,P                                                       R  0198
      FRSUM = FRSUM + CNR(K)                                            R  0204
 30   CONTINUE                                                          R  0210
```

```
      DO 31 K=1,P                                                       R  0210
      FRAC(K) = CNR(K)/FRSUM                                            R  0216
   31 CONTINUE                                                          R  0226
      CALL EXCESS                                                       R  0226
      DO 8 II=1,M                                                       R  0227
      TERM = 1.0                                                        R  0232
      CNRK(II) =1.0                                                     R  0236
      RGNRK(II) = 1.0                                                   R  0244
      DO 7 K=1,P                                                        R  0253
      CNRK(II) = CNRK(II)*FRAC(K)**BETA(II,K)                           R  0259
      RGNRK(II) = RGNRK(II)*RGAM(K)**BETA(I),K)                         R  0281
    7 CONTINUE                                                          R  0304
      DO 19 J=1,S                                                       R  0304
      TERM = TERM*SACTIV(J)**ALPHA(II,J)                                R  0310
   19 CONTINUE                                                          R  0322
      R(II) = (CT(II)-CNRK(II)*RGNRK(II)*TERM)/CT(II)                   R  0322
    8 CONTINUE                                                          R  0353
      GO TO 50                                                          R  0353
   92 MN = N-KPES+1                                                     R  0355
C----------EXTENTS IN SOLUTION MOLES,IN RESIN MOLES                    R  0356
      DO 9 J=1,S                                                        R  0357
      CNS(J) = CONCOJ(J)                                                R  0363
      DO 10 I=1,M                                                       R  0371
      CNS(J) = CNS(J) + ALPHA(I,J)*X(I)/VSLO                            R  0377
   10 CONTINUE                                                          R  0396
    9 CONTINUE                                                          R  0399
      CALL DEBYE                                                        R  0399
      DO 11 K=1,P                                                       R  0400
      CNR(K) = CONCOK(K)                                                R  0406
      DO 12 I=1,M                                                       R  0414
      CNR(K) = CNR(K) + BETA(I,K)*X(I)                                  R  0420
   12 CONTINUE                                                          R  0440
   11 CONTINUE                                                          R  0441
      FRSUM = 0.0                                                       R  0441
      DO 13 K=1,P                                                       R  0443
      FRSUM = FRSUM + CNR(K)                                            R  0449
   13 CONTINUE                                                          R  0455
      DO 14 K=1,P                                                       R  0455
      FRAC(K) = CNR(K)/FRSUM                                            R  0461
   14 CONTINUE                                                          R  0471
```

```
      CALL EXCESS                                                          R  0471
      DO 15 II=1,M                                                         R  0472
      CNSJ(II) = 1.0                                                       R  0477
      SGNSJ(II) = 1.0                                                      R  0486
      CNRK(II) = 1.0                                                       R  0495
      RGNRK(II) = 1.0                                                      R  0504
      DO 16 J=1,S                                                          R  0513
      CNSJ(II) = CNSJ(II)*CNS(J)**ALPHA(II,J)                              R  0519
      SGNSJ(II) = SGNSJ(II) *SGAM(J)**ALPHA(II,J)                          R  0541
16    CONTINUE                                                             R  0564
      DO 17 K=1,P                                                          R  0564
      IF(II-MN)17,18,18                                                    R  0570
18    CNRK(II) = CNRK(II)*FRAC(K)**BETA(II,K)                              R  0574
      RGNRK(II) = RGNRK(II)*RGAM(K)**BETA(II,K)                            R  0596
17    CONTINUE                                                             R  0618
      F(II) = (CT(II)-CNSJ(II)*SGNSJ(II)*CNRK(II)*RGNRK(II))/CT(II)        R  0618
15    CONTINUE                                                             R  0660
50    RETURN                                                               R  0661
      END                                                                  R  0664
                                                    SEGMENT    14 IS   677 LONG
```

```
                                                    START OF SEGMENT **********  15
      SUBROUTINE NELM(X,F,EPS,H)                                           R  0000
      DOUBLE PRECISION X,F,EPS,H,FP,XS,P,DX,DXM,XMIN,XMAX,X1,X2,X3,X4,AL   R  0000
     $PHA,PALPHA,DELTX,DA,DB,DC,F1,F2,F3,F4,TEMP,FF                        R  0000
      DIMENSION X(1),P(1),FP(1),XS(1),H(1),FF(1),F(1)                      R  0000
      KOUT=3                                                               R  0000
      DX=H(1)                                                              R  0000
      DXM = 2.0*DX                                                         R  0004
      X1=X(1)                                                              R  0009
      X2=X1+DX                                                             R  0012
      X3=X2+DX                                                             R  0015
      X(1)=X1                                                              R  0017
      CALL CALFUN(M,N,FF,X)                                                R  0021
      F1 = FF(1)**2.0                                                      R  0024
```

```
      X(1)=X2                                                                    R  0031
      CALL CALFUN(M,N,FF,X)                                                      R  0035
      F2 = FF(1)**2.0                                                            R  0038
      X(1)=X3                                                                    R  0045
      CALL CALFUN(M,N,FF,X)                                                      R  0049
      F3 = FF(1)**2.0                                                            R  0052
      PALPHA = 1.0                                                               R  0059
      ALPHA=(EPS/(1.+EPS))**0.2                                                  R  0062
      DO 100 I9=1,1000                                                           R  0073
      DXM=DXM*0.99                                                               R  0078
      PALPHA=PALPHA*ALPHA                                                        R  0082
      X4=0.5*(((X2+X3)*(X2-X3)*F1 - (X1+X3)*(X1-X3)*F2 + (X1+X2)*(X1-X2)         R  0085
     $*F3)   /   ((X2-X3)*F1 - (X1-X3)*F2 + (X1-X2)*F3))                        R  0096
      DELTX=X4-X3                                                                R  0107
      DA=(F2-F1)/(X2-X1)                                                         R  0110
      DB=(F3-F2)/(X3-X2)                                                         R  0113
      DC=(F3-F1)/(X3-X1)                                                         R  0117
      JA=1                                                                       R  0121
      IF(DA*DB.LE.0.)JA=0                                                        R  0122
      IF(DB*DC.LE.0.)JA=0                                                        R  0126
      IF(DA*DC.LE.0.)JA=0                                                        R  0131
      JB=1                                                                       R  0136
      XMAX=X1                                                                    R  0137
      IF(X2.GT.XMAX)XMAX=X2                                                      R  0138
      IF(X3.GT.XMAX)XMAX=X3                                                      R  0143
      XMIN=X1                                                                    R  0147
      IF(X2.LT.XMIN)XMIN=X2                                                      R  0149
      IF(X3.LT.XMIN)XMIN=X3                                                      R  0153
      IF(X4.LT.XMAX.AND.X4.GT.XMIN)JB=0                                          R  0158
      JC=1                                                                       R  0164
      IF(DA*DELTX.LE.0.)JC=0                                                     R  0165
      IF((1-JA)*(1-JB).NE.1)GO TO 30                                             R  0169
      TEMP=DABS(X3-X1)                                                           R  0173
      IF(TEMP.LT.DABS(X3-X2))TEMP=DABS(X3-X2)                                    R  0176
      IF(TEMP.LT.DXM)DXM=TEMP                                                    R  0182
30    CONTINUE                                                                   R  0187
      IF(JA.EQ.0)GO TO 50                                                        R  0187
      IF(JB.EQ.0)GO TO 50                                                        R  0189
      IF(JC.EQ.0)GO TO 40                                                        R  0191
      X4=X3-0.9*DSIGN(DXM,DELTX)                                                 R  0193
      GO TO 60                                                                   R  0201
```

```
40    TEMP=(DSQRT(DABS(X3-X2))+DSQRT(DABS(X2-X1)))/3                    R  0203
      TEMP=((TEMP+DSQRT(PALPHA*DX))/3.)**2                              R  0209
      DELTX=DELTX+DSIGN(TEMP,DELTX)                                     R  0215
      X4=X3+DELTX                                                       R  0219
50    CONTINUE                                                          R  0222
      IF(DABS(X4-X3).GT.DXM)X4=X3+DSIGN(DXM,DELTX)                      R  0222
60    CONTINUE                                                          R  0230
      X(1)=X4                                                           R  0230
      CALL CALFUN(M,N,FF,X)                                             R  0234
      F4 = FF(1)**2.0                                                   R  0237
      X1=X2                                                             R  0244
      X2=X3                                                             R  0245
      X3=X4                                                             R  0247
      F1=F2                                                             R  0248
      F2=F3                                                             R  0250
      F3=F4                                                             R  0251
      F(1) = F4                                                         R  0253
      TEMP=DABS(DELTX)/(EPS+1.0D-30)                                    R  0257
      IF(TEMP.LT.DX)RETURN                                              R  0264
100   CONTINUE                                                          R  0271
      WRITE(KOUT,3000)X1,X2,X3,F1,F2,F3                                 R  0271
3000  FORMAT(25H NO CONVERGENCE   X VALS ,3E12.5,9H  F VALS ,3E12.5)    R  0295
      RETURN                                                            R  0295
      END                                                               R  0298
                                                        SEGMENT   15 IS  325 LONG

                                                    START OF SEGMENT *********  16
      SUBROUTINE VA02A(M,N,F,X,E,FSCALE,IPRINT,MAXFUN)                  R  0000
      DOUBLE PRECISION F,X,E,ESCALE,XINC,FA,FB,D,DA,DB,DC,W,SUM,B,BB,FF,R  0000
     $CHANGE,DM,FC,ACC,XC,XL,XSTEP,FZ,FMIN,FSEC,SUM2                    R  0000
      COMMON/VD0/XINC,FA,FB,D,DA,DB,DC,IINC                             R  0000
      DIMENSION F(20),X(20),W(400),E(20)                                R  0000
      MPLUSN=M+N                                                        R  0000
      KST=N+MPLUSN                                                      R  0001
      NPLUS=N+1                                                         R  0002
      KINV=NPLUS*(MPLUSN+1)                                             R  0003
      KSTORE=KINV-MPLUSN-1                                              R  0005
      CALL CALFUN(M,N,F,X)                                              R  0007
      NN=N+N                                                            R  0010
      K=NN                                                              R  0011
      DO1 I=1,M                                                         R  0012
```

```
      K=K+1                                                          R  0017
      W(K)=F(I)                                                      R  0019
    1 CONTINUE                                                       R  0028
      IINV=2                                                         R  0028
      K=KST                                                          R  0029
      I=1                                                            R  0030
    2 X(I)=X(I)+E(I)                                                 R  0031
      CALL CALFUN(M,N,F,X)                                           R  0044
      X(I)=X(I)-E(I)                                                 R  0047
      DO 3 J=1,N                                                     R  0060
      K=K+1                                                          R  0065
      W(K)=0.                                                        R  0067
      W(J)=0.                                                        R  0071
    3 CONTINUE                                                       R  0076
      SUM=0.                                                         R  0076
      KK=NN                                                          R  0078
      DO 4 J=1,M                                                     R  0078
      KK=KK+1                                                        R  0084
      F(J)=F(J)-W(KK)                                                R  0086
      SUM=SUM+F(J)*F(J)                                              R  0098
    4 CONTINUE                                                       R  0103
      IF (SUM) 5,5,6                                                 R  0108
    5 WRITE(3,7)I                                                    R  0112
    7 FORMAT(5X,6HVA02A ((,I3,20H) UNREASONABLY SMALL)               R  0122
      DO 8 J=1,M                                                     R  0122
      NN=NN+1                                                        R  0127
      F(J)=W(NN)                                                     R  0129
    8 CONTINUE                                                       R  0135
      GO TO 10                                                       R  0139
    6 SUM=1./DSQRT(SUM)                                              R  0140
      J=K-N+I                                                        R  0144
      W(J)=E(I)*SUM                                                  R  0146
      DO 9 J=1,M                                                     R  0155
      K=K+1                                                          R  0161
      W(K)=F(J)*SUM                                                  R  0163
      KK=NN+J                                                        R  0172
      DO 11 II=1,I                                                   R  0173
      KK=KK+MPLUSN                                                   R  0173
      W(II)=W(II)+W(KK)*W(K)                                         R  0180
   11 CONTINUE                                                       R  0195
```

```
      ILESS=I-1                                                         R  0196
      IGAMAX=N+I-1                                                      R  0197
      INCINV=N-ILESS                                                    R  0199
      INCINP=INCINV+1                                                   R  0200
      IF (ILESS) 13,13,14                                               R  0202
   13 W(KINV)=1.                                                        R  0205
      GO TO 15                                                          R  0209
   14 B=1.                                                              R  0210
      DO 16 J=NPLUS,IGAMAX                                              R  0211
      W(J)=0.                                                           R  0216
   16 CONTINUE                                                          R  0221
      KK=KINV                                                           R  0221
      DO 17 II=1,ILESS                                                  R  0222
      IIP=II+N                                                          R  0227
      W(IIP)=W(IIP)+W(KK)*W(II)                                         R  0229
      JL=II+1                                                           R  0244
      IF (JL-ILESS) 18,18,19                                            R  0245
   18 DO 20 JJ=JL,ILESS                                                 R  0248
      KK=KK+1                                                           R  0253
      JJP=JJ+N                                                          R  0255
      W(IIP)=W(IIP)+W(KK)*W(JJ)                                         R  0256
      W(JJP)=W(JJP)+W(KK)*W(II)                                         R  0271
   20 CONTINUE                                                          R  0287
   19 B=B-W(II)*W(IIP)                                                  R  0288
      KK=KK+INCINP                                                      R  0296
   17 CONTINUE                                                          R  0298
      B=1./B                                                            R  0298
      KK=KINV                                                           R  0302
      DO 21 II=NPLUS,IGAMAX                                             R  0303
      BB=-B*W(II)                                                       R  0308
      DO 22 JJ=II,IGAMAX                                                R  0314
      W(KK)=W(KK)+BB*W(JJ)                                              R  0319
      KK=KK+1                                                           R  0332
   22 CONTINUE                                                          R  0334
      W(KK)=BB                                                          R  0334
      KK=KK+INCINV                                                      R  0339
   21 CONTINUE                                                          R  0341
      W(KK)=B                                                           R  0341
   15 GO TO (27,24),IINV                                                R  0347
   24 I=I+1                                                             R  0353
```

```
      IF (I-N) 2,2,25                                                    R  0354
   25 IINV=1                                                             R  0357
      FF=0.                                                              R  0357
      KL=NN                                                              R  0359
      DO 26 I=1,M                                                        R  0360
      KL=KL+1                                                            R  0365
      F(I)=W(KL)                                                         R  0367
      FF=FF+F(I)*F(I)                                                    R  0375
   26 CONTINUE                                                           R  0385
      ICONT=1                                                            R  0385
      ISS=1                                                              R  0386
      MC=N+1                                                             R  0387
      IPP=IABS(IPRINT)*(IABS(IPRINT)-1)                                  R  0388
      ITC=0                                                              R  0390
      IPS=1                                                              R  0391
      IPC=0                                                              R  0392
   27 IPC=IPC-IABS(IPRINT)                                               R  0393
      IF (IPC) 28,29,29                                                  R  0394
   28 WRITE(3,30) ITC,MC,FF                                              R  0397
   30 FORMAT (//5X,9HITERATION,I4,I9,16H CALLS OF CALFUN,5X,2HF=,E24.14) R  0411
      WRITE(3,31)(X(I),I=1,N)                                            R  0411
   31 FORMAT (5X,9HVARIABLES,/(5E24.14))                                 R  0429
      IF(IPRINT)1000,1001,1001                                           R  0429
 1001 WRITE(3,32)(F(I),I=1,M)                                            R  0432
   32 FORMAT (5X,9HFUNCTIONS,/(5E24.14))                                 R  0450
 1000 IPC=IPP                                                            R  0450
      GO TO (29,33),IPS                                                  R  0450
   29 GO TO (34,35),ICONT                                                R  0457
   35 IF (CHANGE-1.) 10,10,36                                            R  0463
   10 IF(IPRINT)1003,33,37                                               R  0467
 1003 WRITE(3,1002)                                                      R  0472
 1002 FORMAT(//5X,31HVA02A FINAL VALUES OF VARIABLES)                    R  0476
      GO TO 1004                                                         R  0476
   37 WRITE(3,38)                                                        R  0477
   38 FORMAT (//5X,45HVA02A FINAL VALUES OF FUNCTIONS AND VARIABLES)     R  0481
 1004 IPS=2                                                              R  0481
      GO TO 28                                                           R  0481
   33 RETURN                                                             R  0483
   36 ICONT=1                                                            R  0486
   34 ITC=ITC+1                                                          R  0487
      K=N                                                                R  0488
      KK=KST                                                             R  0489
```

```
      DO 39 I=1,N                                                       R  0489
      K=K+1                                                             R  0495
      W(K)=0.                                                           R  0497
      KK=KK+N                                                           R  0501
      W(I)=0.                                                           R  0502
      DO 40 J=1,M                                                       R  0506
      KK=KK+1                                                           R  0512
      W(I)=W(I)+W(KK)*F(J)                                              R  0514
   40 CONTINUE                                                          R  0530
   39 CONTINUE                                                          R  0531
      DM=0.                                                             R  0531
      K=KINV                                                            R  0533
      DO 41 II=1,N                                                      R  0533
      IIP=II+N                                                          R  0539
      W(IIP)=W(IIP)+W(K)*W(II)                                          R  0541
      JL=II+1                                                           R  0556
      IF (JL-N) 42,42,43                                                R  0557
   42 DO 44 JJ=JL,N                                                     R  0560
      JJP=JJ+N                                                          R  0565
      K=K+1                                                             R  0567
      W(IIP)=W(IIP)+W(K)*W(JJ)                                          R  0568
      W(JJP)=W(JJP)+W(K)*W(II)                                          R  0583
   44 CONTINUE                                                          R  0599
      K=K+1                                                             R  0599
43    IF(DM-DABS(W(II)*W(IIP)))45,41,41                                 R  0601
45    DM=DABS(W(II)*W(IIP))                                             R  0612
      KL=II                                                             R  0620
   41 CONTINUE                                                          R  0621
      II=N+MPLUSN*KL                                                    R  0621
      CHANGE=0.                                                         R  0623
      DO 46 I=1,N                                                       R  0624
      JL=N+I                                                            R  0630
      W(I)=0.                                                           R  0632
      DO 47 J=NPLUS,NN                                                  R  0636
      JL=JL+MPLUSN                                                      R  0641
      W(I)=W(I)+W(J)*W(JL)                                              R  0643
   47 CONTINUE                                                          R  0658
      II=II+1                                                           R  0659
      W(II)=W(JL)                                                       R  0659
      W(JL)=X(I)                                                        R  0667
```

```
      IF(DABS(E(I)*CHANGE)-DABS(W(I)))48,48,46                          R  0676
   48 CHANGE=DABS(W(I)/E(I))                                            R  0688
   46 CONTINUE                                                          R  0697
      DO 49 I=1,N                                                       R  0697
      II=II+1                                                           R  0702
      JL=JL+1                                                           R  0704
      W(II)=W(JL)                                                       R  0705
      W(JL)=F(I)                                                        R  0713
   49 CONTINUE                                                          R  0722
      FC=FF                                                             R  0722
      ACC=0.1/CHANGE                                                    R  0724
      IT=3                                                              R  0729
      XC=0.                                                             R  0730
      XL=0.                                                             R  0732
      IS=3                                                              R  0733
      XSTEP = -DMIN1(0.5D 00*ESCALE/CHANGE)                             R  0734
      IF (CHANGE-1.) 50,50,51                                           R  0741
   50 ICONT=2                                                           R  0746
   51 CALL VD01A(IT,XC,FC,6,ACC,1.0D-01,XSTEP,IZ,FZ)                    R  0747
      GO TO (52,53,53,53),IT                                            R  0754
   52 MC=MC+1                                                           R  0762
      IF (MC-MAXFUN) 54,54,55                                           R  0763
   55 WRITE(3,56)MAXFUN                                                 R  0766
   56 FORMAT(5X,5HVA02A,I6,17H  CALLS OF CALFUN)                        R  0776
      ISS=2                                                             R  0776
      GO TO 53                                                          R  0776
   54 XL=XC-XL                                                          R  0778
      DO 57 J=1,N                                                       R  0780
      X(J)=X(J)+XL*W(J)                                                 R  0785
   57 CONTINUE                                                          R  0799
      XL=XC                                                             R  0799
      CALL CALFUN(M,N,F,X)                                              R  0801
      FC=0.                                                             R  0804
      DO 58 J=1,M                                                       R  0805
      FC=FC+F(J)*F(J)                                                   R  0810
   58 CONTINUE                                                          R  0821
      GO TO (59,59,60),IS                                               R  0821
   60 K=N                                                               R  0828
      IF (FC-FF) 61,51,62                                               R  0828
   61 IS=2                                                              R  0835
      FMIN=FC                                                           R  0835
```

```
      FSEC=FF                                                          R  0837
      GO TO 63                                                         R  0838
   62 IS=1                                                             R  0840
      FMIN=FF                                                          R  0840
      FSEC=FC                                                          R  0842
      GO TO 63                                                         R  0843
   59 IF (FC-FSEC) 64,51,51                                            R  0845
   64 K=KSTORE                                                         R  0849
      GO TO (75,74),IS                                                 R  0849
   75 K=N                                                              R  0856
   74 IF (FC-FMIN) 65,51,66                                            R  0857
   66 FSEC=FC                                                          R  0863
      GO TO 63                                                         R  0864
   65 IS=3-IS                                                          R  0866
      FSEC=FMIN                                                        R  0867
      FMIN=FC                                                          R  0868
   63 DO 67 J=1,N                                                      R  0871
      K=K+1                                                            R  0876
      W(K)=X(J)                                                        R  0878
   67 CONTINUE                                                         R  0887
      DO 68 J=1,M                                                      R  0887
      K=K+1                                                            R  0892
      W(K)=F(J)                                                        R  0894
   68 CONTINUE                                                         R  0903
      GO TO 51                                                         R  0903
   53 K=KSTORE                                                         R  0904
      KK=N                                                             R  0904
      GO TO (69,70,69),IS                                              R  0905
   70 K=N                                                              R  0912
      KK=KSTORE                                                        R  0912
   69 SUM=0.                                                           R  0914
      DM=0.                                                            R  0915
      JJ=KSTORE                                                        R  0917
      DO 71 J=1,N                                                      R  0917
      K=K+1                                                            R  0923
      KK=KK+1                                                          R  0925
      JJ=JJ+1                                                          R  0926
      X(J)=W(K)                                                        R  0927
      W(JJ)=W(K)-W(KK)                                                 R  0936
   71 CONTINUE                                                         R  0948
```

```
      DO 72 J=1,M                                                  R  0948
      K=K+1                                                        R  0953
      KK=KK+1                                                      R  0955
      JJ=JJ+1                                                      R  0956
      F(J)=W(K)                                                    R  0957
      W(JJ)=W(K)*W(KK)                                             R  0966
      SUM=SUM+W(JJ)*W(JJ)                                          R  0977
      DM=DM+F(J)*W(JJ)                                             R  0986
   72 CONTINUE                                                     R  0995
      GO TO (73,10),ISS                                            R  0995
   73 J=KINV                                                       R  1001
      KK=NPLUS*KL                                                  R  1001
      DO 76 I=1,KL                                                 R  1003
      K=J+KL*I                                                     R  1008
      J=K+KK                                                       R  1010
      W(I)=W(K)                                                    R  1011
      W(K)=W(J*1)                                                  R  1019
                                                  SEGMENT    16 IS 1023 LONG
                                          START OF SEGMENT **********  17
                                                                   R  0007
   76 CONTINUE                                                     R  0008
      IF (KL-N) 77,78,78                                           R  0011
   77 KL=KL+1                                                      R  0012
      JJ=K                                                         R  0013
      DO 79 I=KL,N                                                 R  0018
      K=K+1                                                        R  0020
      J=J+NPLUS-I                                                  R  0021
      W(I)=W(K)                                                    R  0029
      W(K)=W(J*1)                                                  R  0039
   79 CONTINUE                                                     R  0039
      W(JJ)=W(K)                                                   R  0047
      B=1./W(KL*1)                                                 R  0054
      W(KL*1)=W(N)                                                 R  0063
      GO TO 88                                                     R  0064
   78 B=1./W(N)                                                    R  0071
   88 K=KINV                                                       R  0071
      DO 80 I=1,ILESS                                              R  0077
      BB=B*W(I)                                                    R  0082
      DO 81 J=I,ILESS                                              R  0088
      W(K)=W(K)-BB*W(J)                                            R  0101
      K=K+1
```

```
 81 CONTINUE                                                        R  0103
    K=K+1                                                           R  0103
 80 CONTINUE                                                        R  0105
    IF (FMIN-FF) 82,83,83                                           R  0105
 83 CHANGE=0.                                                       R  0110
    GO TO 84                                                        R  0111
 82 FF=FMIN                                                         R  0113
    CHANGE = DABS(XC)*CHANGE                                        R  0114
 84 XL=-DM/FMIN                                                     R  0117
    SUM = 1./DSQRT(SUM+DM*XL)                                       R  0119
    K=KSTORE                                                        R  0125
    DO 85 I=1,N                                                     R  0126
    K=K+1                                                           R  0131
    W(K)=SUM*W(K)                                                   R  0133
    W(I)=0.                                                         R  0141
 85 CONTINUE                                                        R  0146
    DO 86 I=1,M                                                     R  0146
    K=K+1                                                           R  0151
    W(K)=SUM*(W(K)+XL*F(I))                                         R  0153
    KK=NN+I                                                         R  0166
    DO 87 J=1,N                                                     R  0167
    KK=KK+MPLUSN                                                    R  0173
    W(J)=W(J)+W(KK)*W(K)                                            R  0175
 87 CONTINUE                                                        R  0190
 86 CONTINUE                                                        R  0191
    GO TO 14                                                        R  0191
    END                                                             R  0192
SEGMENT    17 IS   228 LONG
```

```
                                                                    START OF SEGMENT **********  18
      SUBROUTINE VDQIAC(ITEST,X,F,MAXFUN,ABSACC,RELACC,XSTEP,IS,FC)                    R  0000
      DOUBLE PRECISION X,F,ABSACC,RELACC,XSTEP,FC,XINC,FA,FB,D,DA,DB,DC                R  0000
      COMMON/VDQ/XINC,FA,FB,D,DA,DB,DC,IINC                                            R  0000
      GO TO (1,2,2),ITEST                                                              R  0000
    2 IS=6-ITEST                                                                       R  0007
      ITEST=1                                                                          R  0008
      IINC=1                                                                           R  0009
      XINC=XSTEP+XSTEP                                                                 R  0010
      MC=IS-3                                                                          R  0016
      IF(MC)4,4,15                                                                     R  0018
    3 MC=MC+1                                                                          R  0021
      IF(MAXFUN-MC)12,15,15                                                            R  0022
   12 ITEST=4                                                                          R  0025
   43 X=DB                                                                             R  0026
      F=FB                                                                             R  0029
      IF(FB-FC)15,15,44                                                                R  0032
   44 X=DC                                                                             R  0039
      F=FC                                                                             R  0042
   15 RETURN                                                                           R  0047
    1 GO TO (5,6,7,8),IS                                                               R  0050
    8 IS=3                                                                             R  0057
    4 DC=X                                                                             R  0058
      FC=F                                                                             R  0062
      X=X+XSTEP                                                                        R  0066
      GO TO 3                                                                          R  0073
    7 IF(FC-F)9,10,11                                                                  R  0074
   10 X=X+XINC                                                                         R  0084
      XINC=XINC+XINC                                                                   R  0089
      GO TO 3                                                                          R  0094
    9 DB=X                                                                             R  0095
      FB=F                                                                             R  0099
      XINC=-XINC                                                                       R  0104
      GO TO 13                                                                         R  0107
   11 DB=DC                                                                            R  0109
      FB=FC                                                                            R  0112
      DC=X                                                                             R  0117
      FC=F                                                                             R  0121
   13 X=DC+DC-DB                                                                       R  0126
      IS=2                                                                             R  0131
```

```
      GO TO 3                                                           R  0132
    6 DA=DB                                                             R  0133
      DB=DC                                                             R  0136
      FA=FB                                                             R  0140
      FB=FC                                                             R  0143
   32 DC=X                                                              R  0148
      FC=F                                                              R  0152
      GO TO 14                                                          R  0156
    5 IF(FB-FC)16,17,17                                                 R  0158
   17 IF(F-FB)18,32,32                                                  R  0164
   18 FA=FB                                                             R  0170
      DA=DB                                                             R  0173
   19 FB=F                                                              R  0177
      DB=X                                                              R  0181
      GO TO 14                                                          R  0186
   16 IF(FA-FC)21,21,20                                                 R  0187
   20 XINC=FA                                                           R  0193
      FA=FC                                                             R  0196
      FC=XINC                                                           R  0201
      XINC=DA                                                           R  0204
      DA=DC                                                             R  0207
      DC=XINC                                                           R  0211
   21 XINC=DC                                                           R  0215
      IF((D-DB)*(D-DC))32,22,22                                         R  0218
   22 IF(F-FA)23,24,24                                                  R  0226
   23 FC=FB                                                             R  0232
      DC=DB                                                             R  0235
      GO TO 19                                                          R  0238
   24 FA=F                                                              R  0240
      DA=X                                                              R  0244
   14 IF(FB-FC)25,25,29                                                 R  0249
   25 IINC=2                                                            R  0255
      XINC=DC                                                           R  0256
      IF(FB-FC)29,45,29                                                 R  0259
   29 D=(FA-FB)/(DA-DB)-(FA-FC)/(DA-DC)                                 R  0266
      IF(D*(DB-DC))33,33,37                                             R  0279
   37 D=0.5*(DB+DC-(FB-FC)/D)                                           R  0286
      IF(DABS(D-X)-DABS(ABSACC))34,34,35                                R  0299
   35 IF(DABS(D-X)-DABS(D*RELACC))34,34,36                              R  0303
   34 ITEST=2                                                           R  0313
```

```
      GO TO 43
   36 IS=1
      X=0
      IF((DA-DC)*(DC-D))3,26,38
   38 IS=2
      GO TO (39,40),IINC
39    IF(DABS(XINC)-DABS(DC-D))41,3,3
   33 IS=2
      GO TO (41,42),IINC
   41 X=DC
      GO TO 10
40    IF(DABS(XINC-X)-DABS(X-DC))42,42,3
   42 X=0.5*(XINC+DC)
      IF((XINC-X)*(X-DC))26,26,3
   45 X=0.5*(DB+DC)
      IF((DB-X)*(X-DC))26,26,3
   26 ITEST=3
      GO TO 43
      END
```

```
                                                    R  0318
                                                    R  0320
                                                    R  0320
                                                    R  0324
                                                    R  0334
                                                    R  0339
                                                    R  0341
                                                    R  0348
                                                    R  0348
                                                    R  0355
                                                    R  0358
                                                    R  0359
                                                    R  0369
                                                    R  0377
                                                    R  0387
                                                    R  0395
                                                    R  0405
                                                    R  0405
                                                    R  0406
                                  SEGMENT    18 IS   427 LONG
```

```
                                  SEGMENT    19 IS    88 LONG
                                  SEGMENT    20 IS    29 LONG
                                  SEGMENT    21 IS   138 LONG
                        START OF SEGMENT ********** 22
                                  SEGMENT    29 IS     4 LONG
                                  SEGMENT    22 IS    29 LONG

NUMBER OF CARDS = 1039            CORE MEMORY ALLOCATION = 10624 WORDS.

COMPILATION TIME = 55 SECS;       ELAPSED TIME = 74 SECS
```

```
50
 .1000000000000D 04

    NUMBER OF REACTIONS =     1

    REACTION NO.      EQUILIBRIUM CONSTANT
           1               .5248000000000D 01

    REACTION NO.      TOL. ON EXTENT
           1               .1000000000000D-09

 INDEX  SOLUTION SPECIES
   1       SO4
   2       NO3
   3       NA
   4       NASO4

    NUMBER OF SOLUTION SPECIES =     4

INITIAL CONCENTRATION OF SPECIES J
     .9000000000000D-01  .2000000000000D-01  .2000000000000D 00  .0

                                                SPECIES(J)
REACTION(I)
              1     2     3     4
       1    -1.00 0.00-1.00 1.00

IONIC CHARGE OF SPECIES J
   -2.00-1.00 1.00-1.00
```

Table J.2 Solution phase activities for a mixture of Na_2SO_4 and $NaNO_3$.

DEBYE-HUCKEL PARAMETER A OF SPECIES J

.5000000000000D-07 .3000000000000D-07 .4000000000000D-07 .5400000000000D-07

DEBYE-HUCKEL PARAMETER B OF SPECIES J

-.4000000000000D-01 .0 .7500000000000D-01 .0

DEBYE-HUCKEL PARAMETER A AND B

.5085000000000D 00 .3281000000000D 08

VOLUME OF SOLUTION = .1000000000000D 01

EXTENT= .1835363152833D-01 F VALUE= .1113535304282D-38

IONIC STRENGTH OF SOLUTION = .2532927369433D 00

EQUILIBRIUM CONCENTRATION OF SPECIES J IN MOLES PER LITRE SOLUTION

.7164636847167D-01 .2000000000000D-01 .1816463684717D 00 .1835363152833D-01

EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES J IN SOLUTION

.7888550066000D 00 .1101040453960D 00 .1000000000000D 01 .1010404539490D 00

ACTIVITY COEFFICIENTS OF SPECIES J

.2686241238403D 00 .6743111696127D 00 .7326154122203D 00 .7323417318035D 00

ACTIVITY OF SPECIES J IN SOLUTION

.1924594295748D-01 .1348622339225D-01 .1330769291162D 00 .1344113029834D-01

Table J.3 Solution phase activities for a mixture of Na_2SO_4, $NaNO_3$ and NaCl.

```
50
 .1000000000000D 04

    NUMBER OF REACTIONS =     1

    REACTION NO.      EQUILIBRIUM CONSTANT
              1            .5248000000000D 01

    REACTION NO.      TOL. ON EXTENT
              1            .1000000000000D-09

 INDEX  SOLUTION SPECIES

   1       SO4

   2       NO3

   3       CL

   4       NA

   5       NASO4

    NUMBER OF SOLUTION SPECIES =      5

INITIAL CONCENTRATION OF SPECIES J

     .2000000000000D-01  .2000000000000D-01  .1400000000000D 00  .2000000000000D 00  .0

                                          SPECIES(J)
REACTION(I)
              1     2     3     4     5
       1     -1.00 0.00 0.00-1.00 1.00
```

IONIC CHARGE OF SPECIES J

-2.00-1.00-1.00 1.00-1.00

DEBYE-HUCKEL PARAMETER A OF SPECIES J

.50000000C0000D-07 .30000000000000D-07 .35000000000000D-07 .40000000000000D-07 .54000000000000D-07

DEBYE-HUCKEL PARAMETER B OF SPECIES J

-.40000000000000D-01 .0 .15000000000000D-01 .75000000000000D-01 .0

DEBYE-HUCKEL PARAMETER A AND B

.50850000000000 00 .32810000000000 08

VOLUME OF SOLUTION = .10000000000000 01

EXTENT= .4547135739421D-02 F VALUE= .1231284349492D-43

IONIC STRENGTH OF SOLUTION = .2109057285212D 00

EQUILIBRIUM CONCENTRATION OF SPECIES J IN MOLES PER LITRE SOLUTION

.1545286426058D-01 .20000000000000D-01 .14000000000000 00 .1954528642606D 00 .4547135739421D-02

EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES J IN SOLUTION

.1581236920630D 00 .1023264615520D 00 .7162852308600D 00 .10000000000000 01 .2326461552050D-01

ACTIVITY COEFFICIENTS OF SPECIES J

•2876222447026D 00 •6905152724816D 00 •7083857210874D 00 •7415001729495D 00 •7434309963902D 00

ACTIVITY OF SPECIES J IN SOLUTION

•4444587505712D-02 •1381030544963D-01 •9917400095224D-01 •1449283326527D 00 •3380481653479D-02

```
50
 .10000000000000D 04

    NUMBER OF REACTIONS =     2

    REACTION NO.      EQUILIBRIUM CONSTANT
              1            .91201000000000D 02
              2            .52480000000000D 01

    REACTION NO.      TOL. ON EXTENT
              1            .10000000000000D-09
              2            .10000000000000D-09

 INDEX  SOLUTION SPECIES

   1       H

   2       SO4

   3       HSO4

   4       NA

   5       NASO4

   6       NO3

   7       CL

    NUMBER OF SOLUTION SPECIES =      7

 INITIAL CONCENTRATION OF SPECIES J

      .12000000000000D 00  .15000000000000D 00  .0                  .28000000000000D 00  .0

      .20000000000000D-01  .80000000000000D-01
```

Table J.4 Solution phase activities for a mixture of Na_2SO_4, $NaNO_3$, NaCl and H_2SO_4.

SPECIES(J)

REACTION(I)

	1	2	3	4	5	6	7
1	-1.00	-1.00	1.00	0.00	0.00	0.00	0.00
2	0.00	-1.00	0.00	-1.00	1.00	0.00	0.00

IONIC CHARGE OF SPECIES J

1.00 -2.00 -1.00 1.00 -1.00 -1.00 -1.00

DEBYE-HUCKEL PARAMETER A OF SPECIES J

.9000000000000D-07 .5000000000000D-07 .4500000000000D-07 .4000000000000D-07 .5400000000000D-07

.3000000000000D-07 .3500000000000D-07

DEBYE-HUCKEL PARAMETER B OF SPECIES J

.0 -.4000000000000D-01 .0 .7500000000000D-01 .0

.0 .1500000000000D-01

DEBYE-HUCKEL PARAMETER A AND B

.5085000000000D 00 .3281000000000D 08

VOLUME OF SOLUTION = .1000000000000D 01

ITERATION 0 3 CALLS OF CALFUN F= .33814442136331E 00

VARIABLES

.7000000000000E-01 .1000000000000E-01

FUNCTIONS

.5623836063408E 00

VA02A FINAL VALUES OF FUNCTIONS AND VARIABLES

ITERATION 10 58 CALLS OF CALFUN F= .32479055362606E-32
VARIABLES
.7069982676786OE-01 .1927631044075 2E-01
FUNCTIONS
-.3701571408288 0E-16 .43332925670846E-16

IONIC STRENGTH OF SOLUTION = .37004772558280 00

EQUILIBRIUM CONCENTRATION OF SPECIES J IN MOLES PER LITRE SOLUTION

.4930017323214D-01 .6002386279139D-01 .7069982676786D-01 .2607236895592D 00 .1927631044075D-01
.2000000000000D-01 .8000000000000D-01

EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES J IN SOLUTION

.1590205759910D 00 .3872209206800D 00 .2280464030450D 00 .8409794240100D 00 .6217686041100D-01
.6451116317300D-01 .2580446526920D 00

ACTIVITY COEFFICIENTS OF SPECIES J

.7751382709894D 00 .2322222625777D 00 .6871264535289D 00 .7173764120885D 00 .7097825094757D 00
.6405018451826D 00 .6659451529923D 00

ACTIVITY OF SPECIES J IN SOLUTION

.3821445103864D-01 .1393887226070D-01 .4857972123211D-01 .1870370249625D 00 .1368198799807D-01
.1281003690365D-01 .5327561223938D-01

Table J.5 Solution phase activities for a mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4.

```
50
 .10000000000000D 04

    NUMBER OF REACTIONS =     4

    REACTION NO.      EQUILIBRIUM CONSTANT
              1             .91201000000000D 02
              2             .13803800000000D 04
              3             .16218100000000D 05
              4             .52481000000000D 01

    REACTION NO.      TOL. ON EXTENT
              1             .10000000000000D-09
              2             .10000000000000D-09
              3             .10000000000000D-09
              4             .10000000000000D-09

INDEX  SOLUTION SPECIES

  1       H

  2       SO4

  3       HSO4

  4       UO2

  5       UO2SO4

  6       UO2(SO4)2

  7       NA

  8       NASO4
```

INITIAL CONCENTRATION OF SPECIES J

.59300000000000D-01 .36410000000000D 00 .0 .23800000000000D-03 .0

.0 .66890000000000D 00 .0

SPECIES(J)

REACTION(I)

	1	2	3	4	5	6	7	8
1	-1.00	-1.00	1.00	0.00	0.00	0.00	0.00	0.00
2	0.00	-1.00	0.00	-1.00	1.00	0.00	0.00	0.00
3	0.00	-2.00	0.00	-1.00	0.00	1.00	0.00	0.00
4	0.00	-1.00	0.00	0.00	0.00	0.00	-1.00	1.00

IONIC CHARGE OF SPECIES J

1.00 -2.00 -1.00 2.00 0.00 -2.00 1.00 -1.00

DEBYE-HUCKEL PARAMETER A OF SPECIES J

.90000000000000D-07 .50000000000000D-07 .45000000000000D-07 .60000000000000D-07 .0

.60000000000000D-07 .40000000000000D-07 .54000000000000D-07

DEBYE-HUCKEL PARAMETER B OF SPECIES J

.0 -.40000000000000D-01 .0 .0 .0

.0 .75000000000000D-01 .0

DEBYE-HUCKEL PARAMETER A AND B

.50850000000000D 00 .32810000000000D 08

VOLUME OF SOLUTION = .1000000000000D 01

ITERATION 0 5 CALLS OF CALFUN F= .7055516845168E-01
VARIABLES
.47000000000000E-01 .79000000000000E-04 .15000000000000E-03 .11040000000000E 00
FUNCTIONS
-.31672860711459E-02 .19013826161569E 00 .18545233101845E 00 -.10554723413656E-03

VA02A FINAL VALUES OF FUNCTIONS AND VARIABLES

ITERATION 6 33 CALLS OF CALFUN F= .1551194419933E-20
VARIABLES
.46970186086479E-01 .79857855283877E-04 .15077486223595E-03 .11040038850047E 00
FUNCTIONS
.38622387012268E-10 -.67261977241677E-11 -.35486504515529E-11 .12926660883589E-11

IONIC STRENGTH OF SOLUTION = .7771123199560D 00

EQUILIBRIUM CONCENTRATION OF SPECIES J IN MOLES PER LITRE SOLUTION

.1232981391352D-01 .2063480178333D 00 .4697018608648D-01 .7367282480174D-05 .7985785528388D-04

.1507748622359D-03 .5584996114995D 00 .1104003885005D 00

EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES J IN SOLUTION

.2160827340890D-01 .72325899126000D 00 .8231629691600D-01 .2582265316080D-04 .0

.5284726061950D-03 .9787830042500D 00 .1934791389320D 00

ACTIVITY COEFFICIENTS OF SPECIES J

•7509129563530D 00 •17215138486170 00 •6386078629034D 00 •2210552530745D 00 •10000000000000 01

•2210552530745D 00 •70869466208220 00 •66838140540370 00

ACTIVITY OF SPECIES J IN SOLUTION

•9258617017085D-02 •3552309703348D-01 •2999553015686D-01 •1628576493126D-05 •7985785528388D-04

•3332957532884D-04 •3958056934447D 00 •7378956682306D-01

Table J.6 Solution phase activities for a mixture of Na_2SO_4, $NaNO_3$, NaCl, H_2SO_4 and UO_2SO_4.

```
50
 .1000000000000D 04

    NUMBER OF REACTIONS =     4

    REACTION NO.      EQUILIBRIUM CONSTANT
              1            .9129100000000D 02
              2            .1380380000000D 04
              3            .1621810000000D 05
              4            .5248100000000D 01

    REACTION NO.      TOL. ON EXTENT
              1            .1000000000000D-09
              2            .1000000000000D-09
              3            .1000000000000D-09
              4            .1000000000000D-09

INDEX  SOLUTION SPECIES

  1       H
  2       SO4
  3       HSO4
  4       UO2
  5       UO2SO4
  6       UO2(SO4)2
  7       NA
  8       NASO4
  9       NO3
 10       CL
```

NUMBER OF SOLUTION SPECIES = 10

INITIAL CONCENTRATION OF SPECIES J

.11200000000000D 00	.14000000000000 00	.0	.10000000000000D-02	.0
.0	.28600000000000D 00	.0	.80000000000000D-01	.40000000000000D-01

REACTION(I) — SPECIES(J)

	1	2	3	4	5	6	7	8	9	10
1	-1.00	-1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	-1.00	0.00	-1.00	1.00	0.00	0.00	0.00	0.00	0.00
3	0.00	-2.00	0.00	-1.00	0.00	1.00	0.00	0.00	0.00	0.00
4	0.00	-1.00	0.00	0.00	0.00	0.00	-1.00	1.00	0.00	0.00

IONIC CHARGE OF SPECIES J

1.00 -2.00 -1.00 2.00 0.00 -2.00 1.00 -1.00 -1.00 -1.00

DEBYE-HUCKEL PARAMETER A OF SPECIES J

.90000000000000D-07	.50000000000000D-07	.45000000000000D-07	.60000000000000D-07	.0
.60000000000000D-07	.40000000000000D-07	.54000000000000D-07	.30000000000000D-07	.35000000000000D-07

DEBYE-HUCKEL PARAMETER B OF SPECIES J

.0	-.40000000000000D-01	.0	.0	.0
.0	.75000000000000D-01	.0	.0	.15000000000000D-01

DEBYE-HUCKEL PARAMETER A AND B

.50850000000000D 00 .32810000000000D 08

```
 ITERATION    0        5 CALLS OF CALFUN      F=      .22958635973783E 01
 VARIABLES
 .80000000000000E-01     .60000000000000E-03     .30000000000000E-03     .14000000000000E-01
 FUNCTIONS
-.12909462801540E 01    -.46869101415538E 00    -.63422043690032E 00     .86107315616982E-01

 VA02A FINAL VALUES OF FUNCTIONS AND VARIABLES

 ITERATION   12      103 CALLS OF CALFUN      F=      .42153839031128E-22
 VARIABLES
 .64132006816811E-01     .56687962087378E-03     .31757638791650E-03     .18476907663296E-01
 FUNCTIONS
-.24242623200126E-11     .58707982997600E-11     .11404874611886E-11    -.71400763952646E-12

IONIC STRENGTH OF SOLUTION =    .37224434700580 00

EQUILIBRIUM CONCENTRATION OF SPECIES J IN MOLES PER LITRE SOLUTION

     .47867993183400D-01  .56189053123790D-01  .64132006816100D-01  .11554399121010D-03  .56687962086970D-03

     .31757638792030D-03  .26752309233660 00   .18476907663400D-01  .80000000000000D-01  .40000000000000D-01

EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES J IN SOLUTION

     .15166232667000 00   .35605263407500 00   .20319233628100 00   .73216650103000D-03  .0

     .20123832517500D-02  .84760550583000 00   .59541221798000D-01  .25346761639800 00   .12673380819800 00
```

ACTIVITY COEFFICIENTS OF SPECIES J

•77492944301590 00 •23168542789870 00 •68672456916590 00 •27301995342720 00 •10000000000000 01

•27301995342720 00 •71718095811030 00 •70943608044650 00 •63997370379600 00 •66550917981370 00

ACTIVITY OF SPECIES J IN SOLUTION

•37094317296290-01 •13018184816210-01 •44041024750530-01 •31545815098970-04 •56687962086970-03

•86704690639580-04 •19186246767860 00 •13108184951490-01 •51197896303680-01 •26620367192550-01

Table J.7 Fitted resin phase composition for the binary system Amberlite 400, mixture of Na_2SO_4 and $NaNO_3$.

```
10
 .1000000000000D 04

    NUMBER OF REACTIONS =     1

    REACTION NO.      EQUILIBRIUM CONSTANT
              1            .72939000000000 02

    REACTION NO.      TOL. ON EXTENT
              1            .1000000000000D-09

INDEX  SOLUTION SPECIES

  1       SO4

  2       NO3

   SPECIES(J)
REACTION(I)
                1     2
       1       1.00-2.00


INDEX  RESIN SPECIES

  1       SO4

  2       NO3

IONIC CHARGE OF SPECIES J

   -2.00-1.00
```

NUMBER OF RESIN SPECIES = 2

NUMBER OF RESIN REACTIONS = 1

INITIAL MOLES OF SPECIES K IN RESIN

.700000000000D-02 .0

SPECIES(K)

REACTION(I)

	1	2
1	-1.00	2.00

WILSON INTERACTION PARAMETERS FOR RESIN PHASE

SPECIES(K)

	1	2
1	.100000 01	.654190 00
2	.311590 01	.100000 01

VOLUME OF FREE SETTLED RESIN IN SULPHATE FORM = .100000000000D-01

CAPACITY OF RESIN EQUIV. PER LITRE FSR = .140000000000D 01

ACTIVITY OF SPECIES J IN SOLUTION

.271200000000D-01 .247050000000D-01

REACTION NO.	INITIAL GUESS FOR EXTENT
1	.370000000000D-02

EXTENT= .3694039067909D-02 F VALUE= .1047314632695D-23

EQUILIBRIUM MOLES OF SPECIES K

.3305960932091D-02 .7388078135819D-02

EQUILIBRIUM MOLE FRACTION OF SPECIES K IN RESIN

.3091405325057D 00 .6908594674943D 00

EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES K IN RESIN

.4722801331550D 00 .5277198668430D 00

ACTIVITY COEFFICIENT OF SPECIES K IN RESIN

.6475401786083D 00 .8297390699582D 00

ACTIVITY OF SPECIES K IN RESIN

.2001809156338D 00 .5732330920305D 00

EQUILIBRIUM CONCENTRATION OF SPECIES K IN MOLES PER LITRE FREE SETTLED RESIN IN SULPHATE FORM

.3305960932091D 00 .7388078135819D 00

```
10
 .10000000000000D 04

    NUMBER OF REACTIONS =     1

    REACTION NO.      EQUILIBRIUM CONSTANT
            1              .50980000000000D 01

    REACTION NO.      TOL. ON EXTENT
            1              .10000000000000D-09

 INDEX  SOLUTION SPECIES

   1       SO4

   2       HSO4

    SPECIES(J)
REACTION(I)
                  1     2
        1       1.00-2.00


 INDEX  RESIN SPECIES

   1       SO4

   2       HSO4

 IONIC CHARGE OF SPECIES J

    -2.00-1.00
```

Table J.8 Fitted resin phase composition for the binary system Amberlite 400, mixture of Na_2SO_4 and H_2SO_4.

NUMBER OF RESIN SPECIES = 2

NUMBER OF RESIN REACTIONS = 1

INITIAL MOLES OF SPECIES K IN RESIN

.70000000000000D-02 .0

SPECIES(K)

REACTION(I)

	1	2
1	-1.00	2.00

WILSON INTERACTION PARAMETERS FOR RESIN PHASE

SPECIES(K)

	1	2
1	.10000D 01	.98460D 00
2	.28124D 01	.10000D 01

VOLUME OF FREE SEITLED RESIN IN SULPHATE FORM = .10000000000000D-01

CAPACITY OF RESIN EQUIV. PER LITRE FSR = .14000000000000D 01

ACTIVITY OF SPECIES J IN SOLUTION

•3556400000000D-01 •3000200000000D-01

REACTION NO.	INITIAL GUESS FOR EXTENT
1	•1850000000000D-02

EXTENT= •1852337891757D-02 F VALUE= •1726156991862D-22

EQUILIBRIUM MOLES OF SPECIES K

•5147662108243D-02 •3704675783515D-02

EQUILIBRIUM MOLE FRACTION OF SPECIES K IN RESIN

•5815031205526D 00 •4184968794474D 00

EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES K IN RESIN

•7353803011800D 00 •2646196988210D 00

ACTIVITY COEFFICIENT OF SPECIES K IN RESIN

•8591157723829D 00 •6066727225376D 00

ACTIVITY OF SPECIES K IN RESIN

•4995785025566D 00 •2538906412279D 00

EQUILIBRIUM CONCENTRATION OF SPECIES K IN MOLES PER LITRE FREE SETTLED RESIN IN SULPHATE FORM

•5147662108243D 00 •3704675783515D 00

```
10
 .10000000000000D 04

    NUMBER OF REACTIONS =     3

    REACTION NO.      EQUILIBRIUM CONSTANT
              1            .50930000000000D 01
              2            .73818000000000D 04
              3            .41408000000000D 02

    REACTION NO.      TOL. ON EXTENT
              1            .10000000000000D-09
              2            .10000000000000D-09
              3            .10000000000000D-09

 INDEX  SOLUTION SPECIES

   1       H

   2       SO4

   3       HSO4

   4       UO2

   5       UO2SO4

   6       UO2(SO4)2

   7       NA

   8       NASO4
```

Table J.9 Fitted resin phase composition for the quaternary system Amberlite 400, mixture of Na_2SO_4, H_2SO_4 and UO_2SO_4.

SPECIES(J)
REACTION(I)

	1	2	3	4	5	6	7	8
1	0.00	1.00	-2.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	-1.00	0.00	0.00	0.00
3	0.00	1.00	0.00	0.00	0.00	-1.00	0.00	0.00

INDEX	RESIN SPECIES
1	SO4
2	HSO4
3	$UO2(SO4)3$
4	$UO2(SO4)2$

IONIC CHARGE OF SPECIES J

-2.00 -1.00 -4.00 -2.00

NUMBER OF RESIN SPECIES = 4

NUMBER OF RESIN REACTIONS = 3

INITIAL MOLES OF SPECIES K IN RESIN

.70000000000000D-02 .0 .0 .0

SPECIES(K)

REACTION(I)

	1	2	3	4
1	-1.00	2.00	0.00	0.00
2	-2.00	0.00	1.00	0.00
3	-1.00	0.00	0.00	1.00

WILSON INTERACTION PARAMETERS FOR RESIN PHASE

SPECIES(K)

	1	2	3	4
1	.10000D 01	.98460D 00	.48276D 01	.52322D 01
2	.28124D 01	.10000D 01	.28237D 01	.81317D 00
3	.26150D-02	.62344D 00	.10000D 01	.36596D-01
4	.17304D 01	.85263D 00	.17655D 01	.10000D 01

VOLUME OF FREE SEITLED RESIN IN SULPHATE FORM = .1000000000000D-01

CAPACITY OF RESIN EQUIV. PER LITRE FSR = .1400000000000D 01

ACTIVITY OF SPECIES J IN SOLUTION

.92586000000000D-02 .35523000000000D-01 .30000000000000D-01 .16286000000000D-05 .79858000000000D-04

.33330000000000D-04 .39581000000000D 00 .73790000000000D-01

REACTION NO.	INITIAL GUESS FOR EXTENT
1	.14000000000000D-02
2	.70000000000000D-03
3	.37000000000000D-03

ITERATION 0 4 CALLS OF CALFUN F= .56021218221024E-01

VARIABLES

.14000000000000E-02 .70000000000000E-03 .37000000000000E-03

FUNCTIONS

-.21331297508401E 00 .97294464699844E-01 -.32443489648949E-01

VA02A FINAL VALUES OF FUNCTIONS AND VARIABLES

ITERATION 7 35 CALLS OF CALFUN F= .819020669312 46E-15
VARIABLES
.128892425862 34E+02 .785649734600 05E+03 .351143533622 39E+03
FUNCTIONS
.272163925090 34E+07 -.875682747579 79E+08 -.126752541030 62E+08

EQUILIBRIUM MOLES OF SPECIES K

.3788632745605D+02 .2577848507385D+02 .7856497356877D+03 .3511435293273D+03

EQUILIBRIUM MOLE FRACTION OF SPECIES K IN RESIN

.5049305788444D 00 .3435631338290D 00 .1047075825098D 00 .4679870481677D-01

EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES K IN RESIN

.5412332493710D 00 .1841320362400D 00 .2244713530530D 00 .5016336133240D-01

ACTIVITY COEFFICIENT OF SPECIES K IN RESIN

.7391305299621D 00 .6390519943032D 00 .7841663426992D 00 .3098338783169D 00

ACTIVITY OF SPECIES K IN RESIN

.3732096063393D 00 .2195547058425D 00 .8210816202958D-01 .1449982421359D-01

EQUILIBRIUM CONCENTRATION OF SPECIES K IN MOLES PER LITRE FREE SETTLED RESIN IN SULPHATE FORM

.3788632745605D 00 .2577848507385D 00 .7856497356877D-01 .3511435293273D-01

```
50
 .1000000000000D 04

    NUMBER OF REACTIONS =    2

    REACTION NO.      EQUILIBRIUM CONSTANT
              1            .72939000000000D 02
              2            .51040000000000D 01

    REACTION NO.      TOL. ON EXTENT
              1            .10000000000000D-09
              2            .10000000000000D-09

 INDEX  SOLUTION SPECIES

   1       SO4

   2       NO3

   3       CL

    SPECIES(J)
REACTION(I)
                 1     2     3
        1       1.00-2.00  0.00
        2       1.00  0.00-2.00


INDEX  RESIN SPECIES

  1       SO4

  2       NO3

  3       CL
```

Table J.10 Prediction of the resin phase composition for the ternary system Amberlite 400, 0,2 N mixture of Na_2SO_4, $NaNO_3$ and NaCl.

NUMBER OF RESIN SPECIES = 3

NUMBER OF RESIN REACTIONS = 2

INITIAL MOLES OF SPECIES K IN RESIN

.70000000000000D-02 .0 .0

SPECIES(K)

REACTION(I)

	1	2	3
1	-1.00	2.00	0.00
2	-1.00	0.00	2.00

WILSON INTERACTION PARAMETERS FOR RESIN PHASE

SPECIES(K)

	1	2	3
1	.10000D 01	.65419D 00	.21192D 00
2	.31159D 01	.10000D 01	.39121D 00
3	.37355D 01	.24627D 01	.10000D 01

VOLUME OF FREE SETTLED RESIN IN SULPHATE FORM = .10000000000000D-01

CAPACITY OF RESIN EQUIV. PER LITRE FSR = .14000000000000D 01

ACTIVITY OF SPECIES J IN SOLUTION

.22335000000000D-02 .13857000000000D-01 .11366670000000D 00

REACTION NO.	INITIAL GUESS FOR EXTENT
1	.10000000000000D-02

ITERATION 0 3 CALLS OF CALFUN F= .19852743479663E 01
VARIABLES
.10000000000000E-02 .10000000000000E-02
FUNCTIONS
.99433310643788E 00 .99828654273605E 00

VA02A FINAL VALUES OF FUNCTIONS AND VARIABLES

ITERATION 11 99 CALLS OF CALFUN F= .88743464334549E-23
VARIABLES
.21864911414815E-02 .43113161350274E-02
FUNCTIONS
.15686545444695E-11 .25325223303201E-11

EQUILIBRIUM MOLES OF SPECIES K

.5021927234911D-03 .4372982282963D-02 .86226322700550-02

EQUILIBRIUM MOLE FRACTION OF SPECIES K IN RESIN

.3720550406473D-01 .3239772352191D 00 .63881726071620 00

ACTIVITY COEFFICIENT OF SPECIES K IN RESIN

.3266400546034D 00 .8520791966828D 00 .9376856722067D 00

ACTIVITY OF SPECIES K IN RESIN

.1215280787925D-01 .2760542623290D 00 .5990097925319D 00

EQUILIBRIUM CONCENTRATION OF SPECIES K IN MOLES PER LITRE FREE SETTLED RESIN IN SULPHATE FORM

.5021927234911D-01 .4372982282963D 00 .8622632270055D 00

Table J.11 Prediction of the resin phase composition for the quaternary system Amberlite 400, mixture of Na_2SO_4, $NaNO_3$, NaCl and H_2SO_4.

```
10
 .10000000000000D 04

    NUMBER OF REACTIONS =     3

    REACTION NO.       EQUILIBRIUM CONSTANT
              1              .50980000000000D 01
              2              .72939000000000D 02
              3              .51040000000000D 01

    REACTION NO.       TOL. ON EXTENT
              1              .10000000000000D-09
              2              .10000000000000D-09
              3              .10000000000000D-09

 INDEX  SOLUTION SPECIES

   1       H

   2       SO4

   3       HSO4

   4       NA

   5       NASO4

   6       NO3

   7       CL

    SPECIES(J)
REACTION(I)
                1     2     3     4     5     6     7
        1      0.00  1.00-2.00  0.00  0.00  0.00  0.00
        2      0.00  1.00  0.00  0.00  0.00-2.00  0.00
        3      0.00  1.00  0.00  0.00  0.00  0.00-2.00
```

INDEX RESIN SPECIES

1 SO4

2 HSO4

3 NO3

4 CL

IONIC CHARGE OF SPECIES J

-2.00 -1.00 -1.00 -1.00

NUMBER OF RESIN SPECIES = 4

NUMBER OF RESIN REACTIONS = 3

INITIAL MOLES OF SPECIES K IN RESIN

.7000000000000D-02 .0 .0 .0

SPECIES(K)

REACTION(I)

	1	2	3	4
1	-1.00	2.00	0.00	0.00
2	-1.00	0.00	2.00	0.00
3	-1.00	0.00	0.00	2.00

WILSON INTERACTION PARAMETERS FOR RESIN PHASE

```
                                                    SPECIES(K)
                1              2              3              4
        1    .10000D 01.98460D 00.65419D 00.21192D 00
        2    .28124D 01.10000D 01.26912D 01.74146D 00
        3    .31159D 01.27678D 00.10000D 01.39121D 00
        4    .37355D 01.12865D 01.24627D 01.10000D 01

VOLUME OF FREE SETTLED RESIN IN SULPHATE FORM =  .1000000000000D-01

CAPACITY OF RESIN EQUIV. PER LITRE FSR =  .1400000000000D 01

ACTIVITY OF SPECIES J IN SOLUTION

     .3821400000000D-01  .1393900000000D-01  .4858000000000D-01  .1870400000000D 00  .1368200000000D-01

     .1281000000000D-01  .5327600000000D-01

   REACTION NO.      INITIAL GUESS FOR EXTENT
             1            .1000000000000D-02
             2            .1000000000000D-02
             3            .1000000000000D-02

   ITERATION   0        4 CALLS OF CALFUN     F=     .25995824266483E 01
   VARIABLES
   .1000000000000E-02     .1000000000000E-02     .1000000000000E-02
   FUNCTIONS
   .9402431904908E 00     .9326603440457E 00     .9196030948340E 00

   ITERATION  10       98 CALLS OF CALFUN     F=     .1099348643702E-03
   VARIABLES
   .1731912825276E-02     .1763066641143E-02     .1719738097588E-02
   FUNCTIONS
  -.9019662546884E-02    -.3851785523458E-02     .3707330601916E-02

   VA02A FINAL VALUES OF FUNCTIONS AND VARIABLES
```

ITERATION 18 126 CALLS OF CALFUN F= .2384635411703E-18
VARIABLES
.1726415209582E-02 .1761843685711E-02 .1724713245753E-02
FUNCTIONS
-.1852088485743E-09 -.4187372581724E-09 -.1697655212295E-09

EQUILIBRIUM MOLES OF SPECIES K

.1787027858569D-02 .3452830419184D-02 .3523687372174D-02 .3449426491504D-02

EQUILIBRIUM MOLE FRACTION OF SPECIES K IN RESIN

.1463221104473D 00 .2827182752240D 00 .2885200532162D 00 .2824395611124D 00

EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES K IN RESIN

.2552896940800D 00 .2466307442260D 00 .2516919551540D 00 .2463876065360D 00

ACTIVITY COEFFICIENT OF SPECIES K IN RESIN

.4436630146303D 00 .8372773167480D 00 .8183117947249D 00 .9196597878470D 00

ACTIVITY OF SPECIES K IN RESIN

.6491770862814D-01 .2367135988751D 00 .2360993625615D 00 .2597483068523D 00

EQUILIBRIUM CONCENTRATION OF SPECIES K IN MOLES PER LITRE FREE SETTLED RESIN IN SULPHATE FORM

.1787027858569D 00 .3452830419184D 00 .3523687372174D 00 .3449426491504D 00

Table J.12 Prediction of the resin phase composition for the six component system Amberlite 400, 0,4 N mixture of Na_2SO_4, NaCl, $NaNO_3$, H_2SO_4 and UO_2SO_4.

```
10
 .1000000000000D 04

    NUMBER OF REACTIONS =     5

    REACTION NO.       EQUILIBRIUM CONSTANT
              1              .50980000000000D 01
              2              .73818000000000D 04
              3              .41408000000000D 02
              4              .72939000000000D 02
              5              .51040000000000D 01

    REACTION NO.       TOL. ON EXTENT
              1              .10000000000000D-09
              2              .10000000000000D-09
              3              .10000000000000D-09
              4              .10000000000000D-09
              5              .10000000000000D-09

INDEX  SOLUTION SPECIES

  1        H

  2        SO4

  3        HSO4

  4        UO2

  5        UO2SO4

  6        UO2(SO4)2

  7        NA

  8        NASO4

  9        NO3
```

SPECIES(J)
REACTION(I)

	1	2	3	4	5	6	7	8	9	10
1	0.00	1.00	-2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	-1.00	0.00	0.00	0.00	0.00	0.00
3	0.00	1.00	0.00	0.00	0.00	-1.00	0.00	0.00	0.00	0.00
4	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	-2.00	0.00
5	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-2.00

INDEX	RESIN SPECIES
1	SO4
2	HSO4
3	UO2(SO4)3
4	UO2(SO4)2
5	NO3
6	CL

IONIC CHARGE OF SPECIES J

-2.00 -1.00 -4.00 -2.00 -1.00 -1.00

NUMBER OF RESIN SPECIES = 6

NUMBER OF RESIN REACTIONS = 5

INITIAL MOLES OF SPECIES K IN RESIN

.700000000000D-02 .0 .0 .0 .0

SPECIES(K)

REACTION(I)

	1	2	3	4	5	6
1	-1.00	2.00	0.00	0.00	0.00	0.00
2	-2.00	0.00	1.00	0.00	0.00	0.00
3	-1.00	0.00	0.00	1.00	0.00	0.00
4	-1.00	0.00	0.00	0.00	2.00	0.00
5	-1.00	0.00	0.00	0.00	0.00	2.00

WILSON INTERACTION PARAMETERS FOR RESIN PHASE

SPECIES(K)

	1	2	3	4	5	6
1	.100000D 01	.984600D 00	.482760D 01	.523220D 01	.654190D 00	.211920D 00
2	.281240D 01	.100000D 01	.232370D 01	.813170D 00	.269120D 01	.741460D 00
3	.261550D-02	.623440D 00	.100000D 01	.365960D-01	.189040D 01	.230270D 00
4	.173040D 01	.952630D 00	.176550D 01	.100000D 01	.311970D 01	.493120D-01
5	.311590D 01	.276780D 00	.293090D 01	.727800D-02	.100000D 01	.391210D 00
6	.373550D 01	.128650D 01	.492920D 01	.248650D 01	.246270D 01	.100000D 01

VOLUME OF FREE SETTLED RESIN IN SULPHATE FORM = .1000000000000D-01

CAPACITY OF RESIN EQUIV. PER LITRE FSR = .1400000000000D 01

ACTIVITY OF SPECIES J IN SOLUTION

.3709400000000D-01 .1301800000000D-01 .4404100000000D-01 .3154600000000D-04 .5668800000000D-03

.8670500000000D-04 .1918600000000D 00 .1310800000000D-01 .5119800000000D-01 .2662000000000D-01

REACTION NO.	INITIAL GUESS FOR EXTENT
1	.1000000000000D-02
2	.2200000000000D-03
3	.1400000000000D-03
4	.3800000000000D-02
5	.4000000000000D-03

ITERATION 0 6 CALLS OF CALFUN F= .26744162700199E-01
VARIABLES
.10000000000000E-02 .22000000000000E-03 .14000000000000E-03 .38000000000000E-02 .60000000000000E-03
FUNCTIONS
.79770803505242E-01 .11105063493282E 00 .44603487708643E-01 .54877535500047E-01 .55204375469796E-01

VA02A FINAL VALUES OF FUNCTIONS AND VARIABLES

ITERATION 6 29 CALLS OF CALFUN F= .14388844335053E-17
VARIABLES
.10151470877143E-02 .22419715327766E-03 .13685737406141E-03 .38122085625248E-02 .60243385106279E-03
FUNCTIONS
.33216594478030E-09 .10351580464596E-08 .27039932993516E-09 .31564035241605E-09 .29020437457857E-09

EQUILIBRIUM MOLES OF SPECIES K

.98495852493640D-03 .20302941721670D-02 .22419715273210D-03 .13685737436050D-03 .76244171176030D-02
.12048677006680D-02

EQUILIBRIUM MOLE FRACTION OF SPECIES K IN RESIN

.80697339162130D-01 .16634130611580 00 .18368395932060D-01 .11212677807050D-01 .62466588295460 00
.98714398028630D-01

EQUILIBRIUM EQUIVALENT FRACTION OF SPECIES K IN RESIN

.14070840356200 00 .14502101229700 00 .64056329352000D-01 .19551053482900D-01 .54460122268600 00
.86061978619000D-01

ACTIVITY COEFFICIENT OF SPECIES K IN RESIN

.30045487207500 00 .81583827448670 00 .13392421171600 00 .59636651120110 00 .95528334934610 00

ACTIVITY OF SPECIES K IN RESIN

•2424590871462D-01 •1357076041574D 00 •2459972945688D-02 •668686554501 4D-02 •5967329168911D 00

•8207492235974D-01

EQUILIBRIUM CONCENTRATION OF SPECIES K IN MOLES PER LITRE FREE SETTLED RESIN IN SULPHATE FORM

•9849586249364D-01 •2030294172167D 00 •2241971527321D-01 •1368573743805D-01 •7624417117603D 00

•1204867700668D 00

```
BURROUGHS B-5700  FORTRAN  COMPILATION    (MARK XVI.0.02).       TUESDAY, 27/04/76.    12:14 H.     UNIVERSITY OF

                                        NOCOMP /ECPRPSM
                                        ===============

FILE  2 =  INPUT              ,UNIT = READER                                    R  0000
FILE  3 =  OUTPUT             ,UNIT = PRINTER                                   R  0000
                                                          START OF SEGMENT **********   1
      DIMENSION CONCOJ(6),Z(6),DBA(6),DBB(6),SGAM(6),ACTIV(6)                   R  0000
      INTEGER S                                                                 R  0000
      REAL MU,MUHALF                                                            R  0000
C     NO3=1                                                                     R  0000
C     CL=2                                                                      R  0000
C     NA=3                                                                      R  0000
      READ(2,100)S,N                                                            R  0000
 100  FORMAT(2I5)                                                               R  0012
      READ(2,400)(Z(J),J=1,S)                                                   R  0012
      READ(2,200)(DBA(J),J=1,S)                                                 R  0029
      READ(2,200)(DBB(J),J=1,S)                                                 R  0046
      READ(2,200)DHA,DHB                                                        R  0063
      WRITE(3,1004)DHA,DHB                                                      R  0074
1004  FORMAT(1X,"DEBYE COEFF ARE",2E10.5)                                       R  0087
200   FORMAT(4E10.5)                                                            R  0087
400   FORMAT(6F5.2)                                                             R  0087
      WRITE(3,1001)                                                             R  0087
1001  FORMAT(1X,"SPECIES",5X,"CHARGE",5X,"DEBYE PARAMS")                        R  0091
      DO 2 J=1,S                                                                R  0091
      WRITE(3,1000)J,Z(J),DBA(J),DBB(J)                                         R  0096
1000  FORMAT(2X,I2,8X,F5.2,2X,E10.5,2X,E10.5)                                   R  0116
2     CONTINUE                                                                  R  0116
      DO 10 I=1,N                                                               R  0116
      WRITE(3,1002)                                                             R  0121
1002  FORMAT(//1X,"SPECIES",5X,"CONCENTRATION",5X,"ACTIVITY COEFF",5X,"A       R  0126
     $CTIVITY",5X,"IONIC STRENGTH")                                             R  0126
      READ(2,200)(CONCOJ(J),J=1,S)                                              R  0126
      SMU=0.0                                                                   R  0143
      DO 1 J=1,S                                                                R  0143
      SMU=SMU+CONCOJ(J)*Z(J)**2.0                                               R  0149
1     CONTINUE                                                                  R  0156
```

Table J.13 Solution phase activities of species in the non-complexing system mixture of NaCl and $NaNO_3$.

```
      MU = 0.5*SMU                                                                    R  0156
      MUHALF = SQRT(MU)                                                               R  0160
      DO 3 J=1,S                                                                      R  0161
      SGAM(J)=10.0**(-1.0*(DHA*MUHALF*Z(J)**2.0)/(1.0+DHB*DBA(J)*MUHALF)              R  0166
     $+DBB(J)*MU)                                                                     R  0182
      ACTIV(J) = SGAM(J)*CONCOJ(J)                                                    R  0185
      WRITE(3,1003)J,CONCOJ(J),SGAM(J),ACTIV(J),MU                                    R  0189
1003  FORMAT(2X,I2,9X,E10.5,6X,E10.5,6X,E10.5,6X,F10.5)                               R  0211
3     CONTINUE                                                                        R  0211
10    CONTINUE                                                                        R  0212
      STOP                                                                            R  0212
      END                                                                             R  0214
                                                          SEGMENT    1 IS  233 LONG
```

```
DEBYE COEFF ARE.50850E 00.32810E 08
SPECIES     CHARGE      DEBYE PARAMS
  1        -1.00   .30000E-07   .0
  2        -1.00   .35000E-07   .15000E-01
  3         1.00   .40000E-07   .75000E-01

SPECIES     CONCENTRATION     ACTIVITY COEFF      ACTIVITY      IONIC STRENGTH
  1         .10000E-01        .69518E 00        .69518E-02      .20000E 00
  2         .19000E 00        .71245E 00        .13536E 00      .20000E 00
  3         .20000E 00        .74422E 00        .14884E 00      .20000E 00

SPECIES     CONCENTRATION     ACTIVITY COEFF      ACTIVITY      IONIC STRENGTH
  1         .20000E-01        .69518E 00        .13904E-01      .20000E 00
  2         .18000E 00        .71245E 00        .12824E 00      .20000E 00
  3         .20000E 00        .74422E 00        .14884E 00      .20000E 00

SPECIES     CONCENTRATION     ACTIVITY COEFF      ACTIVITY      IONIC STRENGTH
  1         .40000E-01        .69518E 00        .27807E-01      .20000E 00
  2         .16000E 00        .71245E 00        .11399E 00      .20000E 00
  3         .20000E 00        .74422E 00        .14884E 00      .20000E 00
```

APPENDIX K

LIST OF FIGURES AND TABLES

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